MSEL

Materials Science and Engineering Laboratory

POLYMERS

NISTIR 5315
U.S. Department of Commerce
Technology Administration
National Institute of Standards
and Technology

Technical Activities
1993

Computer simulation of a chemically reactive polymer blend undergoing phase separation via spinodal decomposition. Regions rich in one polymer are shown in black and those rich in the other as gray. A balance between the demixing thermodynamics and mixing reactive processes results in novel, equilibrium pattern formation similar to that observed during microphase separation of diblock copolymers. The simulation was performed on a massively-parallel Connection Machine CM-5.

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L.E. Smith, Chief
B.M. Fanconi, Deputy

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1993

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Ronald H. Brown, Secretary

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Certain commercial materials and equipment are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology (NIST) nor does it imply necessarily the best available for the purpose.

INTRODUCTION

POLYMERS DIVISION

Leslie E. Smith, Chief
Bruno M. Fanconi, Deputy Chief

The Polymers Division is responsible for providing standards, measurement methods, and fundamental concepts of polymer science to assist U. S. industries that produce or use synthetic polymers in essential parts of their business. We have a long history of direct collaboration with industry on individual projects and we have used such collaborations as a method of project selection as well as a way of insuring that the work we do has value to our customers. These collaborations have been generally on an individual company basis. Five years ago NIST was given broader responsibility to promote U. S. economic growth through the development and application of technology. Since that time the Polymers Division has focussed its resources more strongly on specific industrial sectors. This focus has allowed us to assess the needs of an industry group and plan responses that are appropriate to our capabilities and role. Program priorities are established by attempting to evaluate the potential payoff to individual companies, the industry sector and to the economy as a whole.

One of our first such efforts began when we chose to look at the potential for fiber reinforced polymer composites within the automotive industry. Through a series of workshops, the industrial need was established for more rapid and less costly processes and our program in liquid molding processes was planned. Such processes inject a reactive polymer into a mold containing a fiber preform. We now have a working model of the flow of polymers in liquid molding processes that predicts the pressures and flow front positions in the mold. This kind of modeling capability allows the more rapid and cost effective production of composite parts. The process of holding regular workshops that assess the needs of the industry in implementing a new technology also gives us a mechanism to measure our impact and to make decisions on changes in direction in our programs.

This year we began a technical effort in electronic packaging and interconnect technology that was planned in the same way. Workshops and discussions with electronics manufacturers first pointed out the critical role that packaging technology now plays in electronics. The packaging is the link that provides the high density interconnections that allow the increased functionality found in modern semiconductor designs to be used in practical and relatively inexpensive consumer and business electronics. The packaging and interconnection aspects of the electronics industry have also received relatively little attention as the primary concern has centered on the intense international competition in the production of the semiconductor chips themselves. There were even concerns that crucial pieces of next generation packaging and printed wiring board technology would not be available in the

U. S. These issues have led us to look at the role of materials in electronic packaging and to develop programs that provide measurement and modeling support to the electronics industry.

Our most comprehensive program aims at the producers and processors of polymer blends. Here we hope to provide the measurement methods and fundamental understanding that will help producers develop new blend systems more quickly. This year we began working with a consortium of interested companies to help guide our research efforts and to transfer our technology more quickly and efficiently to the companies ready to implement it. We continue to seek more participation in this activity. The consortium has allowed us to consolidate a number of one to one interactions so we can deal with a larger number of customers without additional staff. By effectively training the industry participants to use our facilities and analysis methods we can still retain the flexibility to address the unique questions of each of the companies while continuing a core research program that provides general solutions to the problems they have in common.

The blends program aims to provide support also to the formulators and processors of blends. We have begun activities to develop sensors and models of mixing phenomena that could be applied to process control. This is an ambitious project that will begin with the fundamental principles of polymer phase behavior that we have elucidated in simple shear fields and try to apply them to the complexities of practical mixers and extruders.

In all these programs, collaboration with others continues to be the most effective way to develop and transfer technology. In particular, industry collaborators who know both their business and technical needs are vital to planning and execution. Many of these interactions are briefly described in the section on Industrial and Academic Interactions in the Appendix to this report.

All of the Division's programs are described in this report, organized according to these six Groups:

ELECTRONIC APPLICATIONS
POLYMER BLENDS & PROCESSING
POLYMER COMPOSITES
STRUCTURE & MECHANICS
POLYMER CHARACTERIZATION
DENTAL MATERIALS AND DEVICES

These Groups have made a number of significant accomplishments during the last year. Some of these are summarized below along with references to the pages of the report where more information about the work may be found.

- A working group with representatives from U.S. electronics firms, private electronics industry consortia, universities, and other government agencies has been established to improve the metrology used by U.S. firms for characterizing the properties of polymers used in advanced microelectronic packaging. The initial effort has concentrated on out-of-plane thermal expansion of thin films. (pages 4,5)

- Neutron and X-ray reflectivity from the interface of polymers with silicon over a range of temperatures indicate that thin films of polystyrene exhibit a lower T_g than that of the bulk, while the T_g of polymethylmethacrylate is not affected. The effect is believed to correlate with the energy of adhesion. (page 4)

- A NIST/Industry Consortium on Polymer Blends and Alloys, formed in 1993, currently has five industrial members and another six companies and Sandia National Laboratories are in the process of joining. Dialogue with potential industrial partners was carried out through two workshops and numerous discussions. The research effort will focus on measurements of key factors which control the morphology and morphological stabilization. Fundamental knowledge obtained from these studies can be used to guide new product development and development of intelligent processing systems for on-line control. (pages 24,25)

- Self-organization of structure in polymer blends via spinodal decomposition was studied for a deuterated polybutadiene/protonated polyisoprene system. Using a combined time-resolved small-angle neutron scattering and light scattering technique, spatial and time scales of over 4 orders of magnitude can be covered which provide measurements of the evolution in real time of global, interfacial, "interphase", and local structures. (page 18)

- A workshop of industry, university, and government experts in liquid composites molding (LCM) was organized and hosted by NIST. The attendees identified critical challenges that must be addressed to improve the LCM processing method, and these will be used to help plan future directions in the NIST program. (pages 28,29)

- In cooperation with the Automotive Composites Consortium (Ford, General Motors, and Chrysler), a design was developed to instrument a mold for fabrication of a structural automotive part, the cross member in a van. This part is very complex so the mold provides an excellent tool to investigate structural reaction injection molding, and to test the Division's process simulation models. Previous work in this cooperative program has used these simulation models to describe mold filling for other structural automotive parts. (pages 37,38)

- While conducting permeability measurements for the Automotive Composites Consortium (Ford, General Motors, and Chrysler), a material with the principal axes of the permeability tensor tilted out of the plane of the fabric was discovered. Until now, this possibility has not been seriously considered, and thus the current measurement procedures cannot characterize the permeability of such a material. We believe that many more examples of this behavior will be found as more complex preforms are constructed. To address this problem, a new software analysis package has been developed and appropriate experimental equipment and methods are currently being designed. (pages 34,35)

- A new analysis has been developed which allows both the fiber and interface strengths to be estimated from each experiment in the single-fiber fragmentation test. The fiber strength is needed to estimate the interface strength from fragmentation results, but the fiber strength is difficult and time consuming to measure independently. Consequently, the new analysis is a major advance, particularly for studies like moisture attack where the water degrades both the fiber and interface strength. (pages 40,41)

- A Cooperative Research and Development Agreement with Dow Chemical Company to study fracture incubation in engineering thermoplastics using SAXS and Positron Annihilation Lifetime Spectroscopy was signed in September, 1993. (page 49)

- Swelling measurements on the natural rubber/benzene and poly(dimethyl siloxane)/benzene systems using our sub-ambient pressure isopiestic facility confirm prior results from this laboratory that the Flory-Huggins interaction parameter χ is crosslink dependent. The temperature dependence of $\Delta\chi$ has been explored and found to have a very strong temperature and crosslink dependence. There is no current theoretical understanding of this behavior. (pages 61,62)

- Absolute molecular weight measurements on narrow molecular weight distribution polyethylene oxides were made and resulted in certification of two standard reference materials to be used as calibration standards for aqueous size exclusion chromatography (SEC). (page 72)

- A bis-spiro orthocarbonate (SOC) monomer, capable of polymerization with expansion, has provided crosslinked, glassy polymers with near complete double ring opening. This represents a significant advance in the development of expanding monomers since prior to this, SOC homopolymers have been characterized by excessive leachable components, poor mechanical strength, and low glass transition temperatures. (pages 79,80)

RESEARCH STAFF

Antonucci, Joseph M.	o Synthetic and polymer chemistry o Dental composites, cements and adhesion o Antioxidants
Barnes, John D.	o Gas and vapor transport in polymers o X-ray scattering o Computer applications in polymer measurements
Bauer, Barry J.	o Polymer synthesis o Neutron, x-ray and light scattering o Dendrimers
Bennett, Patricia S.[•]	o Synthetic and polymer chemistry o Nuclear magnetic resonance
Blair, William R.	o Ultratrace metals speciation o Polymer analysis by size exclusion chromatography o Environmental durability of coatings
Bowen, Rafael L.[•]	o Adhesion o Dental composites o Biocompatibility
Briber, Robert J.[+]	o Structure and morphology of polymers o Electron microscopy o X-ray scattering
Broadhurst, Martin G.[+]	o Dielectric measurements o Piezoelectric and pyroelectric modeling and theory o Equation of state of polymers o Ionic conduction
Bur, Anthony J.	o Dielectric properties of polymers o Fluorescence and optical monitoring of polymer processing o Piezoelectric, pyroelectric polymers o Polymeric transducers

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Campbell, Jr., Gordon C.[+]	o Solid state NMR of polymers o Off-resonance proton irradiation techniques
Carey, Clifton M.[*]	o Dental plaque o Microanalytical analysis techniques
Chang, Shu Sing[+]	o Thermal properties of polymeric and composite materials o Composite process monitoring o Electronic packaging materials o Polymer phase transitions o Precision electrical and temperature measurements
Chiang, Martin Y.	o Computational mechanics (finite element analysis) o Strength of materials o Engineering mechanics of polymer based materials
Chow, Lawrence C.[*]	o Calcium phosphate compounds o Dental and biomedical cements o Solution chemistry o Topical dental fluorides
Dadmun, Mark D.	o Liquid-crystalline polymers o Polymer Gelation o Light and neutron scattering
Davis, G. Thomas	o Electronic packaging o Polymer crystallization o X-ray diffraction of polymers o Polarization distribution o Piezoelectricity in polymers
DeReggi, Aime S.	o Polarization-depth profiles in polymers o Space charge in dielectrics o Ferroelectric polymers o Polymeric piezo- & pyroelectric devices

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Di Marzio, Edmund A.	o Statistical mechanics of polymers o Phase transitions o Glasses o Polymers at interfaces
Dickens, Brian	o Polymer oxidation o Monomer design and free radical curing o Automation o Photoacoustic spectroscopy
Dickens, Sabine*	o Clinical dentistry o Dental composites o Dental polymers
Douglas, Jack F.	o Theory on polymer solutions and blends o Polymers at interfaces o Scaling and renormalization group calculation
Dunkers, Joy P.	o Polymer characterization o Vibrational spectroscopy of polymers o Fiber optics spectroscopy o Process monitoring
Eanes, Edward D.*	o Structure of bones and teeth o Calcium phosphate compounds o Effects of biological molecules on precipitation of calcium phosphates o Liposome studies
Eichmiller, Frederick C.*	o Clinical dentistry o Composites o Dentin adhesives
Eidelman, Naomi N.*	o Atherosclerotic plaque
Fanconi, Bruno M.	o Infrared & Raman spectroscopy of polymers o Structure of polymers o Polymer fracture o Process monitoring of polymer composites

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Farahani, Mahnaz*	o Radiation chemistry/physics o Analytical chemistry
Feng, Yi+	o Temperature jump light scattering o Phase separation kinetics of polymer blend
Flynn, Kathleen M.	o Permeability Measurements o Flow Visualization Experiments
Fowler, Bruce O.*	o Infrared and laser Raman structural analysis of calcium phosphates
Giuseppetti, Anthony A.*	o Casting of dental alloys o Titanium alloys
Glotzer, Sharon C.	o Parallel processing simulations of blends
Guttman, Charles M.	o Solution properties of polymers o Size exclusion chromatography o Semicrystalline polymer chain configurations o Kinetics of polymer crystal growth
Hailer, Arthur W.*	o Chemical reactions, chemical analysis
Han, Charles C.	o Phase behavior of polymer blends o Phase separation kinetics of polymer blends o Polymer characterization o Polymer diffusion o Small angle neutron scattering o Static and quasi-elastic light scattering
Hoffman, Kathleen M.*	o Synthetic and polymer chemistry o Adhesion
Horkay, Ferenc+	o Rubber thermodynamics o Gels

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Hunston, Donald L.	o Adhesion science and technology o Fracture behavior of polymers o Processing and failure behaviors of polymer composites o Flow behavior of dilute high polymer solutions o Macromolecular-small molecule binding
Ishikawa, Kunio*	o Calcium phosphate compounds
Jackson, Catheryn L.	o Structure and morphology of polymers and polymer blends o Transmission and scanning electron microscopy o Finite-size effects on crystalline melting and glass transition temperatures o Liquid crystalline polymers o Microcellular foams morphology
Jewett, Kenneth L.	o Redox kinetics of heterogeneous systems o Organometallic speciation o Abiotic transformation of metal species o Analysis of organic mixtures o Diffusion and absorption of gases in polymeric matrices
Johnsonbaugh, David S.	o Atomic absorption spectrophotometry o Microbiology
Johnston, Allen D.*	o Nuclear magnetic resonance o Mossbauer studies o Chemical adhesion
Karim, Alamgir	o Thin film phase behavior o Blends o Block copolymer o Neutron reflection, scattering o X-ray reflection
Keeny III, Spurgeon M.+	o Gas plasma sterilization o Mechanical testing o Tribiology, dental materials o Fluorescence studies

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Khoury, Freddy A.[+]	o Crystallization, structure and morphology of polymers (including polymer blends) o Analytical electron microscopy of polymers o Wide angle and small angle x-ray diffraction o Structure and mechanical property relationships
Kryder, Samuel J.	o Electronic circuit design and construction o Electronic troubleshooting and repair
Kurakawa, Hidenobu[+]	o Polymer solution thermodynamics o Small angle neutron scattering
Liu, D.-W.	o Monomer synthesis o Polymer and polymer composites
Lowry, Robert E.	o Applications of fluorescence spectroscopy to polymeric systems o Synthesis of chromophore-labeled polymers
Ly, Agnes M.[*]	o Clinical dental assistant o Adhesion measurements
Mao, Yu[+]	o Dental plaque o Microanalytical techniques
Mathew, Mathai[*]	o Crystallography o Calcium phosphate compounds
Maurey, John M.	o Ultracentrifugation o Rayleigh light scattering o Osmometry o Densimetry o Refractometry o Intrinsic viscosity
McDonough, Walter G.	o Processing and cure monitoring polymer composites o Failure and fracture of polymers o Microstructure characterization of polymer composites

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McKenna, Gregory B.	o Failure, yield and fracture of polymers o Nonlinear viscoelasticity o Molecular rheology o Physics of polymer glasses o Rubber thermodynamics and mechanics o Mechanics of composites
McKinney, John E.[+]	o Tribiology of dental composites, cements and alloys
Migler, Kalman	o Polymer solutions under shear o Surface rheology o Liquid crystal dynamics o Fluorescence and light scattering
Misra, Dwarika N.[*]	o Surface chemistry o Adhesion o Chemisorption
Moon, Chang-Kwon[+]	o Fiber-matrix interface in composites
Mopsik, Frederick L.	o Dielectric measurements and behavior o Automated measurement design o Computerized data analysis and programming o Electrical properties of polymers
Nachlis, Warren L.	o Phase behavior & morphology of polymer blends o Structure property relationships o Polymer deformation behavior o Reactive processing
Nakatani, Alan I.	o Polymer blends and solution properties under shear o Small angle neutron scattering o Phase behavior of polymer blends
O'Farrell, Thomas J.[*]	o Mineralization and remineralization
Orts, William J.	o Neutron and x-ray scattering o Polymer morphology and crystallization o Mechanical properties of polymers

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Parnas, Richard S.	o Flow through porous media with heterogeneous structure o Surface rheology o Polymer dynamics
Phelan, Jr., Frederick R.	o Resin transfer molding: modeling and processing studies o Viscoelastic flow modeling o Engineering rheology
Ranganathan, Sridhar[+]	o Computerized modeling of fluid flow o Process simulation models for composites
Ratzker, Menahem B.[*]	o Electrodeposition
Reed, Benjamin B.[*]	o Synthetic and polymer chemistry o Polymerization expanding monomers
Roth, Steven C.	o Piezoelectric polymer transducers-fabrication and applications o Vacuum deposition of metals o Calibration of polymer transducers o Microcomputer interfacing o Fluorescence measurements
Rupp, Nelson W.[*]	o Clinical dentistry o Amalgams o Direct golds o Composites o Microleakage o Dentin adhesives
Sakurai, Shinichi[+]	o Polymer blends o Equilibrium and kinetics of phase separation o Light scattering
Sanin, Norman D.[*]	o Topical dental fluorides

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Schadt, Randall J.	o NMR of polymers o Pulsed field gradient NMR o Moisture in polymers
Schen, Michael A.	o Polymers for non-linear optics o Optical spectroscopy o metrology of microelectronic materials
Schutte, Carol L.	o Surface chemistry o Polymer composite interfaces
Schultheisz, Carl R.	o Failure of composites o Experimental mechanics
Shioya, Masatosi[+]	o Fiber surface science o Fiber-matrix interface
Sieck, Barbara A.[*]	o Calcium phosphate compounds o Chemical analysis
Smith, Leslie E.	o Adsorption of polymers o Polymer degradation reactions
Stansbury, Jeffrey W.	o Synthetic chemistry o Polymers and polymer composites o Polymerization expanding monomers
Takagi, Shozo[*]	o Crystallography o X-ray diffraction o Calcium phosphate compounds
Terech, Pierre[+]	o Small angle X-ray and neutron scattering o Physical gelation

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Tesk, John A.	o Bond strength characterization o Casting of alloys o Strength of dental systems o Thermal expansion and properties of dental materials o Finite element studies o Porcelain-metal system o Weibull analysis o Gas plasma sterilization
Tomazic, Branko*	o Atherosclerotic plaque o Biological calcium phosphate compounds
Tung, Ming A.*	o Biological solution chemistry of calcium phosphate compounds o Equilibrium studies
VanderHart, David L.	o Measurement of orientation in polymer fibers and films o Solid state NMR of polymers o Measurement of polymer morphology at the 2-50 nm scale o Structure of asphalt cements and concretes o Pulsed field gradient NMR
Van Zanten, John H.	o Complex fluids o Polymer interfaces o Scattering of light, neutrons & x-rays o Biophysics
Verdier, Peter H.	o Polymer solution properties o Polymer chain dynamics in solution o Statistical analysis of data o Error estimation o Computer simulation of polymer chain dynamics
Vogel, Gerald L.*	o Dental plaque, biological solution chemistry of calcium phosphates o Microanalytical techniques
Waldron, William K.	o Nonlinear viscoelasticity o Mechanics and thermodynamics of rubber

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Wallace, William E.	o Surface and interface behavior o Ion beam and electronic spectroscopies o X-ray and neutron reflectivity
Wang, Francis W.	o Photophysics and photochemistry of polymers o Fluorescence spectroscopy o Thermodynamic and frictional properties of macromolecules
Winnert, Laurie A.[*]	o Glass-ceramics
Woerdeman, Dara[+]	o Permeability o Composite process monitoring
Wu, Wen-li	o Neutron and x-ray scattering o Electron microscopy o Mechanical behavior of polymers and composites

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TECHNICAL ACTIVITIES

ELECTRONICS APPLICATIONS

The mission of this group is to characterize and evaluate the properties of polymers to be used in electronic applications, such as microelectronic packaging, high energy density capacitors, electro-optics, and piezoelectrics. Many of the applications for these polymers are as thin films, often adhered to a substrate, so that thin film properties and interfacial interactions are of particular interest. In response to the needs of industry or other government agencies, a main activity in this group is the improvement of existing measurement techniques and the development of new ones. For example, in recent years, improvements have been made to the NIST-developed time domain dielectric spectrometer as well as the thermal pulse instrumentation for measuring the distribution of charge or polarization across the thickness of thin dielectric films. Neutron reflectivity and grazing incidence X-ray reflectivity are applied to study the silicon/polymer interface as well as the polymer/air interface. Assessment of the reproducibility and reliability of measurements frequently required for electronic packaging materials is being pursued in collaboration with a group from the microelectronics industry as well as universities and other government agencies.

The packaging of modern microelectronics involves the intimate interaction of inorganics, metals, and organic polymers. Predicting the stresses that develop at such interfaces in a package design as a result of temperature changes and the mismatch of thermal expansion coefficients requires accurate data on the thermal and mechanical properties of all components, particularly in the same form as exists in the end use. The properties of polymers such as polyimides commonly employed in microelectronic packaging depend not only upon the chemical composition but also upon the curing conditions and molecular orientation. A high temperature oven has been installed which will allow reproducible curing conditions in a controlled atmosphere. Photoacoustic infrared spectroscopy is explored as a means of evaluating the degree of cure as well as a means of depth profiling polyimide films adhered to an opaque substrate. A program has been initiated that will compare several techniques for monitoring the stress developed at a polyimide-silicon interface as a result of cooling from cure temperatures in the vicinity of 400°C. For example, stresses deduced from beam bending or wafer warpage will be compared with those obtained from piezoresistive elements built into the single crystal silicon wafer.

Organic polymers with highly polarizable side chains offer great potential for non-linear optical (NLO) applications, such as optical switches, harmonic generators, and modulators. Polar groups which have the potential NLO properties must be preferentially aligned for device applications. One promising method to achieve orientation is with electric fields, just as in the case of polymers which exhibit piezoelectric and pyroelectric properties. Uniformity of the polarization (and therefore refractive index) across the thickness of the waveguide will become an important variable which needs to be measured in connection with the performance of optical devices made from such polymers. The thermal pulse technique developed for measuring the distribution of polarization in piezoelectric and pyroelectric films can be applied equally as well to films of interest in non-linear optics. A guest scientist from the University of Sao Paulo at Sao Carlos, Brazil has been measuring polarization distribution in films of the alternating copolymer of vinylidene cyanide and vinyl acetate, a potential host polymer for NLO molecules, as a function of poling conditions.

Electrical measurements continue to be a strong component of the group's capabilities. The time domain dielectric spectrometer which covers the range of frequencies from 10^{-3} to 10^{4} Hz has been converted to a user-friendly, menu-driven, PC-based system. Dielectric measurements in the range from 1 MHz to 1 GHz are made on a commercially available impedance analyzer. A computer-controlled system for evaluating electrical energy recovery from capacitor films at well controlled rates of discharge has been constructed as well as a system for measuring current-voltage hysteresis loops on ferroelectric polymers.

FY 93 Significant Accomplishments

- A computer-controlled oven has been installed and made operational which will allow the high temperature curing of polyimides under reproducible conditions of temperature and time in controlled atmospheres.

- A working group with representatives from U.S. electronics firms, private electronics industry consortia, universities, and other government agencies has been established to improve the metrology used by U.S. firms for characterizing the properties of polymers used in advanced microelectronic packaging. The initial effort has concentrated on out-of-plane thermal expansion of thin films.

- Neutron and X-ray reflectivity from the interface of polymers with silicon over a range of temperatures indicate that thin films of polystyrene exhibit a lower T_g than that of the bulk, while the T_g of polymethylmethacrylate is not affected. The effect is believed to correlate with the energy of adhesion.

- A new low frequency relaxation process in polyolefin electrical insulation subjected to gamma radiation has been discovered by time-domain dielectric spectroscopy.

NEUTRON AND X-RAY REFLECTIVITY

Wen-li Wu, John Van Zanten, William J. Orts,
William E. Wallace, III, and Pearl Chin[1]

[1] University of Delaware, Newark, DE

Theoretical Developments

Progress has been made in both the development of off-specular scattering theory and in the conduct of experimental work critical to validating the theory. The theory, once completed, will enable the determination of both in-plane and out-of-plane structural information of buried interfaces from reflectometry data. The theoretical development is based on a two-potential approach with a distorted wave approximation for modelling the scattering wavefunction. To demonstrate the validity of our theoretic work, a set of x-ray measurements were conducted using samples of monodispersed gold particles, 200Å in diameter, adhered to silicon wafers. The results of a series of transverse scans at a fixed 2θ of 1.92 degree is given in Figure 1a where the off-specular intensity is plotted vs. the grazing incident angle. The lowest curve was from the bare surface and the three successively higher intensity curves were from samples with 3%, 6% and 12% surface coverage, respectively. The theoretical result, without the specular component and the finite resolution correction, is given in Figure 1b. The main characteristics of the experimental data are reproduced by the theory. The computer code to correct for finite resolution is under development.

Water Adsorption at Polyimide/Silicon Wafer Interface

Water is one of the most detrimental agents attacking interfaces within composites, adhesive joints and multilayer electronic modules. Water-accelerated degradation is especially severe when high surface energies are involved. Metal surfaces in adhesive bonds, fiber glass surfaces in composites and silicon oxide layers in electronic packages are some common examples of high energy surfaces. The previous annual report described the first use of neutron reflectivity (NR) to quantify the water content and thickness of a moisture enriched layer at a polyimide/silicon interface. A two micrometer thick film of polyimide (a random copolymer based on 3,4'-benzophenone tetracarboxylicdianhydride, 4,4'-oxydianiline and m-phenylene diamine) on silicon single crystal wafers was prepared by spin-coating. The NR results unambiguously pointed to the presence of a moisture rich layer about 25Å thick at the PI/Si interface in a sample exposed to deuterium oxide. The heavy water content within this thin layer reached 16% by volume.

Work has been extended to explore the effect of a silane coupling agent on the moisture adsorption at PI/Si interfaces. γ-aminopropyltrimethoxy silane, a commonly used coupling agent in the electronics industry, was spin-coated onto the silicon wafer prior to the polyimide. Again, the neutron reflectivity results indicate the existence of a thin water-rich layer at the interface, the moisture concentration reaches a maximum of 12% compared with 16% for the sample without the silane coupling agent. This result clearly demonstrates that this silane coupling agent does not completely expel all the water from the PI/Si interface. The most noticeable difference in the D_20 concentration profiles occurs in the ~10Å region immediately next to the silicon wafer, where the presence of silane molecules lowers the water level by about 50%. Between 10Å and 25Å away from the silicon wafer, the silane effect is less pronounced, but still reduces the water concentration by about 25 percent. The silane has no effect at larger distances.

Glass Transition Temperature of Polymers near Interfaces

In order to probe the mobility of long chain molecules adhered to a flat surface, the glass transition temperatures, T_g, of thin polymer films were determined using x-ray reflectivity (XR) and NR measurements. T_g was identified with the temperature where a sudden change in the slope of the thermal expansion of film thickness took place. Film thicknesses ranged from values below the radius of gyration of individual molecules to values above the radius of gyration. Polystyrene (PS) and poly(methyl methacrylate) (PMMA) spin coated on silicon wafers were studied.

Measurements on PS/silicon wafer indicated that the molecules in the thin films started to shrink upon heating at temperatures far below T_g of bulk PS. At elevated temperatures thermal expansion was observed; the linear thermal expansion coefficient in the film thickness direction was close to that of the bulk value. In other words, T_g of a thin PS film on a silicon wafer is lower than its bulk value. For PMMA, the NR results indicated that its T_g does not depend on the film thickness. Difference in the work of adhesion of PMMA vs PS on silicon wafer is believed to be the reason for this observed discrepancy. Work is in progress to quantify the work of adhesion between various polymer/substrate pairs.

Work is also in progress to include metal surfaces as substrates, for example, aluminum and chromium surfaces have been prepared. Since these metal surfaces are subject to oxidation, depth profiles of oxygen in both aluminum and chromium thin films have been determined using a combination of x-ray and neutron reflectivity data. The depth resolution is in the range of a few angstroms.

ELECTRONICS PACKAGING MATERIALS METROLOGY

Michael A. Schen, Fred I. Mopsik, G. Thomas Davis, Will Guthrie[1]

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Thermal Mechanical Analysis

Since February, 1993, NIST's Polymers Division has been working closely with members of the microelectronics manufacturer and user industries in a project intended to improve the quality and sophistication of metrology used by U.S. firms for characterizing properties of polymers used in advanced packaging applications. Participants in the measurements project include individual U.S. corporations, private electronics industry consortia, universities, and other government agencies.

The present activities of the project focus on the improvement of measurement techniques used to determine the coefficient of thermal expansion (CTE) of polymer films in the range of 50-100 micrometers thickness. The CTE of individual components within a microelectronic module and the extent to which they each differ determine the degree to which internal stresses build in the module upon manufacture and use and the propensity for them to fail at interfaces. Consequently, accurate and reliable tools for measuring the CTE of polymers are critically important for improving package reliability and chip durability.

Using a distributed research and development approach, the project has been conducting round-robin measurements of 50 micrometer thick polyimide films as a means of refining the methods and methodologies used by researchers for determining CTE using the thermal mechanical analyzer (TMA). Existing testing methods for determining CTE of polymers by TMA issued by the Semiconductor Equipment and Materials International (SEMI), the Institute for Interconnecting and Packaging Electronic Circuits (IPC), and the American Society for Testing and Materials (ASTM) have proved to be inadequate and have been shown to yield CTE results that vary by as much as 50% across the participants in this NIST project. Presently, a testing method is being developed that utilizes standard silicon chips for standardization of test results and determining the influence of experimental testing factors on instrument response and repeatability. The final goal of the present exercise is to introduce through the appropriate standards organizations an improved standard test method for CTE by TMA of polymer films that will provide more reliable results and allow the testing practitioner to determine associated errors.

Advanced Measurement Methods

In advanced electronic and optical packaging applications, the thermal-mechanical properties of materials and structures on a very fine scale dominate the modeling and prediction of the reliability of the electronic or opto-electronic module. This NIST project aims to accelerate the development of advanced measurement methods for the characterization of global and local strain within micron-scale polymer structures. This project complements the work being undertaken within the NIST-Industry materials metrology project (Thermal Mechanical Analysis, above) and seeks to accelerate the introduction of improved metrology within the U.S. microelectronics industry.

The initial focus of this project is to examine the impact of experimental conditions and configurations, and their associated errors, in measurements of the coefficient of thermal expansion (CTE) of thin polymer films in the out-of-plane direction (z-axis) using capacitance-based techniques. The main feature of the method is the development of a mechanically stable electrode that has a well defined electrical area and is properly shielded as a three-terminal capacitor. Such an electrode has a capacitance that is accurately proportional to its separation from a reference larger electrode. By placing the specimen to be measured as a spacer under the guard electrode so that it does not contribute to the measured capacitance, the thermal expansion can be resolved to the accuracy to which a capacitance can be measured. Based upon preliminary work with electrodes on hand, when corrected for the dielectric constant of air derived from temperature, pressure and relative humidity, the capacitance can be measured with a precision of 1×10^{-6}. One should expect a corresponding precision in the relative thickness of the sample. The development of capacitance-based test methods for determining the relative thickness of films is being studied in more detail.

Interfacial Stress

Polyimide layers on silicon, or other inorganic substrates, are basic structures used in microelectronics and microelectronic packaging. One method of preparing these layers is by spin-coating polyamic acid on the substrate, curing at high temperature to convert the polyamic acid to polyimide, and cooling to room temperature. Because of the dissimilar thermal contraction coefficients of the polyimide and the substrate, residual stresses are produced at the polyimide-substrate interface. The stresses depend on the type of polyimide and the cure cycle. In chips and multichip modules where local stresses are amplified by boundary conditions such as sharp corners, residual interfacial stress is believed to be an important reliability issue. In this project, evaluations are made of different polyimides as well as different cure cycles and post-treatments with respect to minimizing residual interfacial stress and maximizing adhesion. New measurement methods for interfacial strain are being sought that offer convenience, accuracy and means for cross-checking and calibration to allow efficient evaluation of different types of polyimides and different cure cycles. The methods use whole-wafer test structures and can be designed to measure anisotropic contraction associated with molecular ordering of the polyimide in the interfacial plane.

Although the main driving force for developing the above-described whole-wafer test structures and appropriate test methods is to investigate quantitatively stress-cure relations for different types of polyimides, the measurement techniques themselves may prove useful in the industry. Two techniques which are being investigated are described below (see A & B). Results will be compared to those obtained with commercial instruments used in the industry to evaluate stress.

A. Split-capacitance probe.

A test structure under study is a 100-μm thick, 50.82-mm (2-inch) diameter, silicon wafer with a 100-nm thick aluminum electrode on one entire surface. The opposite surface is available to receive a spin-coated, high temperature-cured polyimide layer. This test wafer is mounted with its electroded face parallel to and at a small spacing from, a pair of identical electrodes deposited on a rigid glass plate within the projected area of the wafer. Different electrode patterns are used for different purposes as discussed later. One pattern consists of thin circular arcs, 180° apart, with centers coaxial with the wafer center. The capacitance between the glass-borne electrodes is monitored. This capacitance comes from the series combination of the two capacitors formed by each glass-borne electrode and the wafer-borne electrode. As the polyimide cures, the wafer warps causing a change in the average distance between the arc electrodes and the wafer electrode measured as a capacitance change. The nominal shape of the warped wafer is that of a dome.

The glass-borne electrodes pattern determines what parts of the wafer contribute to the capacitance change. The thin arcs pattern centered on the wafer gives the gap change at a fixed radial distance from the wafer center. For this pattern, parallelism errors are averaged circumferentially. A radial line pattern gives the radially-averaged gap change. The use of more than one set of electrodes would allow sampling different parts of the deformed wafer at the same time.

Both wafer and glass are mounted horizontally to allow the initial gap between wafer and glass to be set by small silicon spacers providing rim support of the wafer under its own weight. The contributions to the capacitance change by the wafer weight and electrode with temperature-dependent flexure moduli are subtracted by obtaining capacitance data before and after spin-coating the polyimide.

The above-described arrangement uses polyimide on crystalline silicon not only because it simulates stress in silicon-on-silicon devices but also because silicon is a good elastic material (negligible hysteresis in the stress-strain curve) with good thermal conductivity (nominally the same as aluminum). The results should still be useful for analyzing stress in copper-polyimide on ceramic devices and for improving multilayered interconnects.

B. Integrated piezoresistive semiconductor strain gage.

Direct measurement of strain within the wafer itself is an alternative to the capacitive measurement of wafer warpage. This is accomplished by integrating piezoresistive patterns within silicon test wafers following the well known techniques of fabricating semiconductor strain gages. Specialized test structures with integrated strain gages have recently been produced at the chip level by investigators at Sandia and in several industrial laboratories for various purposes, but no test wafers suitable for our purposes are available commercially.

A prototype test wafer is in the planning stage. Boron implantation and photolithography will be used to generate piezoresistive patterns on silicon [100] wafers at the NIST semiconductor processing facility. The patterns will consist of closely spaced double lines designed to measure radial or tangential strain at different radial distances. Double lines (or any even numbers of lines) reduce ac pick-up from noise generators such the 60-Hz power line. Radial patterns have piezoresistive coefficients depending on their orientation with respect to the crystallographic axes but may sample radially- varying strain in which case the piezoresistive response will be proportional to the average of the radially varying stress. Arc patterns have coefficients determined by the average of the angle-dependent piezoresistive coefficient along the arc path. The piezoresistive response could then be the product of both the average strain and the average piezoresistive coefficient.

Calibration of the wafer-integrated strain gages will be accomplished at a level consistent with requirements for ranking polyimide types and curing cycles. Comparison with capacitance measurements and with measurements made with a commercial non-contact surface topographer available at NIST (a scanning-sample interference microscope) are expected to be adequate for our purposes. Surface-mounted silicon membrane strain gages procured commercially will also be used. Although these perturb the measured strain, they could be used at temperatures up to the curing temperature. The well known temperature dependence of the piezoresistive effect in silicon will be subtracted in runs where the temperature is varied using data obtained prior to spin- coating the polyimide or by using differential measurements on coated and uncoated but otherwise matched wafers.

Theoretical models of a warped wafer are being developed to provide insights about the expected behavior of the strain and provide a basis for evaluating experimental data. The theory of plates and shells developed extensively in textbooks is being adapted to account for the composite nature of the deforming spin-coated wafer.

PHOTOACOUSTIC SPECTROSCOPY AND CURE OF POLYIMIDES

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Polymers are widely used in electronic packaging to provide low dielectric constant films which insulate the metal conductors. Among the requirements for such a film are that it should: 1) initially be tractable so that the film can be deposited on the substrate, 2) cure to become inert to the solvents and conditions used in the depositing of successive films, 3) adhere to the substrate, to previously-deposited inert films, and to the metal conductors, 4) have anisotropic thermal expansion so that adhesion to dissimilar materials such as substrate and metal conductors can be accommodated, 5) be stripable if reworking is necessary, 6) planarize rough structures, and 7) be stable at temperatures which allow soldering to be carried out.

For various reasons, polyimides have been generally used to produce such films. They are usually deposited from solvent as precursors containing ionic (acid) or labile (ester) groups. Upon heating, the precursor forms chemical bonds of the imide type. The cure of a polyimide entails chemical changes which render a soluble material insoluble and heat resistant, and physical changes in which no new chemical bonds are formed but the order in the solid increases and its properties become more anisotropic. The chemical cure continues until, as a result of the formation of large rigid structures, the remaining reactive groups are not mobile enough to meet one another. Physical ordering also takes place to the extent permitted by the mobility of the polyimide moieties. However, the system does not attain equilibrium. The state achieved depends on the precursor itself, its concentration in the solvent, the rate of loss of solvent and any reaction products (of which water is typically one), and the time spent at each temperature of the cure cycle.

Although the limits on the properties of a polyimide are governed by its chemical composition, the state of cure of the polyimide governs the extent to which these properties are realized. Therefore, polyimide films should be cured in a reproducible way and the degree of cure should be monitored. Measurements of cure should follow the chemical and physical transformation in film specimens 5 to 25 μm thick as typically used in micro-electronic packaging. If feasible, the degrees of chemical cure and physical ordering should be separated as a function of film thickness in these measurements.

Infrared Photoacoustic spectroscopy (PAS) has been investigated as a method of following changes during the cure of polyimides. Three polyamic acid solutions were heated at 2°C/min and 20°C/min in nitrogen or air to give the corresponding polyimides, characterized as flexible, semi-flexible and semi-rigid, respectively. Although PAS can conveniently probe polyimide films down to a depth of about 20 μm, only very weakly-absorbed parts of the spectrum allow penetration that far into the specimens. An algorithm was devised to reveal 1) those parts of the spectrum which are useful in assessing whether different amounts of orientation are induced during slow cure and fast cure, 2) whether there are effects of oxidation by curing in the presence of air rather than nitrogen, and 3) if the presence of a sublayer, similar but not identical in composition to the top layer, can be discerned under a top layer of about 5 μm thickness. The results show that physical ordering in the flexible polyimide is not affected by the rate of cure for rates in the range of 2 to 20°C/min, whereas orientation changes are easily seen in the other two less flexible polyimides. Oxidation effects were noticed for all three polyimides. A sublayer could easily be seen through about 5 μm of top layer, even for materials of quite similar chemical composition. Methods of quantifying these differences between polyimide layers using the PAS spectra have been proposed.

DIELECTRIC RELAXATION MEASUREMENTS

Fred I. Mopsik

The time domain dielectric spectrometer became fully operational this fiscal year and has been used quite heavily. One such use, that has resulted in a publication in press, is the study of radiation-damaged polymeric electrical insulation. This study showed that the use of single-frequency data in the range of 10 to 1000 Hz can indeed be misleading and inconsistent. The inconsistency results from a lack of a complete picture of the loss in the frequency region below 10 kHz despite the appearance of a new loss region that appears in this frequency range and seems to parallel the radiation damage to the polymer. This new loss region is independent from the relaxation processes found in these polymers and is easily detected in a Cole-Cole representation.

Another investigation using the spectrometer has been a determination of the relaxation behavior of polyisobutylenes in conjunction with a guest worker, Dr. Reiner Zorn. These studies were made in parallel with mechanical relaxation measurements in the Polymers Division and used to study the implications of mode-coupling theory. The measurements were made over a wide range of temperatures down to -100°C as well as degree of vinyl content. This latter variation allowed control of the glass transition temperature. The dielectric data were found to be inconsistent with stretched exponential behavior as expected from mode coupling theory. Also, the loss in the sub T_g relaxation did not fit any conventional model.

A paper has been written on the stability of a numerical transform of time-domain data into the frequency-domain. It showed that the uncertainty of the time-domain data from all sources directly translates into the frequency domain with almost no change in error. This work shows that there is no inherent instability in the process for any arbitrary relaxation mechanism. Also, a manuscript has been prepared that sets tight bounds on the number of data points needed to transform time-domain data into the frequency domain. These bounds include both the time interval as well as the point density. This work provides a much firmer basis for the analysis of the main approximation proposed by others.

SPACE CHARGE AND POLARIZATION PROFILES

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Thermal Pulse Developments

The thermal pulse method is probably best suited among charge-profiling methods for measuring charge in dielectric films with thicknesses in the micrometer and submicrometer ranges. In concert with the Division's growing interest in dielectric problems in microelectronics, a collaboration has been established with partners at MIT Lincoln Labs and in NIST's EEEL to evaluate the usefulness of the thermal pulse method for measuring the charging behavior of buried silicon oxide layers (SIMOX structures). The first measurements on SIMOX structures done in the Division with the Lincoln Lab partner demonstrated the feasibility of observing signals from 100 nm thick oxide layers. Follow-up measurements at Lincoln Labs have shown a consistent dependence of the signals on the sign and amplitude of an applied bias voltage. These preliminary data indicate strongly inhomogeneous charge distributions across the SIMOX structures. Interpretation of these data requires reworking the heat flow equations in keeping with the unusual structures.

Polarization Profiles in Optically Non-linear Materials

Although a number of polymers have shown non-linear optical (NLO) properties comparing favorably with those of the best inorganic crystals, the thickness-direction profiles of the polarization induced by poling and the stability of this polarization are still major problems. The problem is most severe if the polymer is a host material for dissolved NLO molecules and is ameliorated if the NLO molecule is chemically grafted to the polymer chain or if the neat polymer itself is the NLO-active material. High glass-transition temperature (T_g) and strong quasi-stable internal fields are thought to be favorable factors for good orientational stability of the NLO species.

A thermal pulse study has been made of the poling behavior, the polarization profile induced by poling, and the thermal stability of this polarization in a copolymer of vinylidene cyanide and vinyl acetate, P(VDCN-VAc), a promising candidate material for NLO applications. P(VDCN-VAc) is amorphous, a desirable property for low light scattering, and has shown second order NLO properties after poling. It further has a high T_g starting around 170°C and strong paraelectric properties above T_g with a polarization that can be made quasi-stable at ambient temperature by a thermopoling process. The thermal pulse data show virtually no polarization unless the poling temperature is above 150°C. For higher poling temperatures, a polarization linear on the applied voltage is observed, and the polarization profile is highly nonuniform and consistent with positive charge injection (or negative charge ejection). Thermal pulse data on thermopoled samples of P(VDCN-VAc) isothermally aged for up to 30 days show excellent thermal stability of the polarization for aging temperatures up to 150°C. The results also show that poling variables can be adjusted to make the polarization profile nearly uniform.

POLYMER BLENDS AND PROCESSING

The goal of the Polymer Blends and Processing Group is to assist the polymer industry by developing fundamental understanding, measurement techniques, data, and process control methods for mixing processes and control of morphology of polymers and polymer blends.

Processing is one of the most important steps in the manufacturing of plastic products. Due to more stringent requirements in the properties and dimensional stability for new applications and in new product development, together with the complex nature of multiphase processing in polymer blends/alloys, a more scientifically disciplined approach in process design and control has become the key issue in gaining competitiveness in the 1990's. Although the growth in the total annual production and in new product development has remained strong in the late 1980's and early 1990's for polymer blends/alloys, the challenge of responding to specific customer/market needs while reducing the new-product development cycle, can only be met through a more scientific and systematic approach, instead of the trial-and-error approach mostly used in the 80's (see Plastics Technology, June, 1992).

Research of this group is focused on the fundamental understanding and control of factors which determine the stability of phases, the kinetics of phase separation, sensor development, and process modeling and control. The emphasis is on mixing processes of single polymer component systems with/without additives or multi component polymer blends/alloys. The science/technology involved can be summarized to include: (1) Thermodynamics of polymer blends; (2) Kinetics of phase separation and crystallization; (3) Shear mixing/demixing and phase separation kinetics after cessation of flow; (4) Interfacial modification and control; (5) Mixing/demixing of reactive blends; and (6) Development of sensor/detector and control technology.

Experimental and theoretical studies relevant to polymers and polymer blends are actively pursued. Measurement techniques employed in the group include small angle neutron scattering (SANS), time resolved SANS, in-situ shear SANS, time resolved temperature-jump light scattering (TJLS), shear light scattering, conventional elastic light scattering, dynamic light scattering, optical and electron microscopies, and various kinds of fluorescence monitoring and measurements. A new shear device with both time resolved light scattering and optical microscopy/image analysis detection systems is under construction.

FY 93 Significant Accomplishments

- NIST/Industry Consortium on New Measurement Technology for Polymer Processing was formally initiated in 1992. Currently, there are six industrial members besides NIST. The direct interaction with industry provided the framework for defining the consortium research program. This program emphasizes the development of new in-line measurement technology for polymer processing based on optical and fluorescence methods.

- NIST/Industry Consortium on Polymer Blends and Alloys, formed in 1993, currently has five industrial members and another six companies and Sandia National Laboratories are in the process of joining. Dialogue with potential industrial partners was carried out through two workshops and numerous discussions. The research effort will focus on measurements of key factors which control the morphology and morphological stabilization. Fundamental knowledge obtained from these studies can be used to guide new product development and development of intelligent processing systems for on-line control.

- Self-organization of structure in polymer blends via spinodal decomposition was studied for a deuterated polybutadiene/protonated polyisoprene system. Using a combined time-resolved small-angle neutron scattering and light scattering technique, spatial and time scales of over 4 orders of magnitude can be covered which provide measurements of time evaluation of global, interfacial, "interphase", and local structures.

- Structural stabilization of phase separating PC/polyester blends through interfacial modification by transesterification has been studied by time resolved small-angle neutron scattering and DSC techniques. This temperature dependent process of structure growth/dissolution with simultaneous transesterification provides a reactive compatibilization technique for polymer alloying. The intricate balance of structure growth and transesterification rates controls the global and interfacial structure. The DSC measurements provided information on the composition of the discrete phase.

EXPERIMENTAL AND THEORETICAL STUDIES

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1. Equilibrium Phase Behavior

Thermodynamic Interactions in Model Polyolefin Blends Obtained by Small-Angle Neutron Scattering: The dependence of the Flory-Huggins interaction parameter, χ, on temperature, composition, and chain length was investigated for binary blends of amorphous model polyolefins, materials which are structurally analogous to copolymers of ethylene and 1-butene. The components were prepared by saturating the double bonds of nearly monodisperse polybutadienes (78%, 88%, and 97% vinyl content) with H_2 and D_2, the latter to provide contrast for small-angle neutron scattering (SANS) experiments. Values of χ were extracted from SANS data in the single-phase region for two series of blends, H97/D88 and H88/D78, using the random-phase approximation and the Flory-Huggins expression for free energy of mixing. These values were found to be insensitive to chain length (one test only) and to the component volume fractions for $\phi = 0.25$, 0.50, and 0.75. Their temperature dependence (27-170°C) obeys the form $\chi(T)=A/T+B$ with coefficients that connote upper critical solution behavior, yielding $T_c \sim 40°C$ for one blend series (H97A/D88) and $T_c \sim 60°C$ for the other (H88/D78). These estimates are consistent with SANS pattern changes and supplemental light scattering results that indicate two-phase morphologies at lower temperatures. The $\chi(T)$ coefficients for the two series are also consistent with the random copolymer theory.

Thermodynamic Interactions and Correlations in Mixtures of Two Homopolymers and a Block Copolymer by Small Angle Neutron Scattering: Thermodynamic interactions in mixtures of two homopolymers and a block copolymer were obtained from small-angle neutron scattering (SANS) measurements. Experimental SANS profiles from homogeneous, ternary mixtures of model polyolefins- poly(ethyl butylene)/poly(methyl butylene)/poly(methyl butylene)b-poly(ethyl butylene) - were compared with theoretical predictions based on the multi-component random phase approximation (RPA). The polymers were nearly monodisperse, and were synthesized by saturating the double bonds in anionically synthesized polydienes with H_2 and D_2, thus yielding polyolefins with neutron scattering contrast. The theoretical scattering profiles depend on 16 structural parameters and 6 Flory-Huggins interaction parameters, χ, all of which were obtained independently. The χ parameters were obtained from SANS measurements on binary poly(ethyl butylene)/poly(methyl butylene) blends. The SANS profiles obtained from the ternary blends were in quantitative agreement with the theoretical predictions over the observable q-range (0.008 to 0.04 Å^{-1}), and over a wide range of block copolymer concentrations (from 10 to 80 volume % copolymer). This suggests that the measured χ parameters are consistent with the original ideas of Flory and Huggins, that χ is a measure of monomer-monomer interactions, and is thus independent of block copolymer concentration. Partial structure factors, related to correlations in the concentration of individual components, were examined by selective labeling, and were also found to be in quantitative agreement with the predictions of the multi-component RPA.

Dynamic Light-Scattering Study of a Diluted Polymer Blend Near Its Critical Point: The critical dynamics of a relatively-high-molecular-weight asymmetric critical polymer blend (polystyrene/polybutadiene) in DOP solution was investigated by dynamic light scattering. Two essentially diffusive decay rates were observed, which are interpreted as the "normal modes" of a pseudo-binary fluid. In the temperature range studied, the data are consistent with an interpretation in terms of a crossover from mean-field to Ising-type mode-coupling dynamics. Dilution of the polymer blend increases the temperature range in which Ising-type (Fisher renormalized) critical behavior is exhibited. The slow mode exhibits sensitivity to perturbations of the polymer solution.

Asymptotic Crossover in Polymer Blends: Susceptibility and specific-heat data for a low-molecular-weight polymer blend (polybutadiene/polystyrene) near its critical point of unmixing are compared with a match-point renormalization-group theory which describes the crossover from classical mean-field to fluctuation-dominated behavior near the critical temperature. The C_p data are in reasonable agreement with the behavior expected from a fit of the susceptibility, but it is impossible to determine whether there is crossover to critical behavior based on heat-capacity data alone, as the size of the observed anomaly is the same as the predicted mean-field jump. This is consistent with the susceptibility being the strongest measure of the importance of critical fluctuations. Perhaps the best measure of the width of the critical regime in this blend can be found in its response to shear flow as measured with small-angle neutron scattering, which very strongly suggests that critical fluctuations do not become significant until roughly 5 degrees away from T_c as described in our previous work.

Localization of a Homopolymer Dissolved in a Lamellar Structure of a Block Copolymer Studied by Small-Angle Neutron Scattering: The localization of deuterated styrene homopolymer dissolved in a lamellar structure of a styrene-2-vinylpyridine diblock copolymer was compared to that of the end-part of the block copolymer by observing diffraction from the styrene and 2-vinylpyridine microdomains of deuterated styrene homopolymer/styrene-2-vinylpyridine diblock copolymer blends by small-angle neutron scattering (SANS). Even when the average scattering lengths of both domains were equal, that is, "phase contrast matching" was theoretically achieved, diffraction was definitely observed. From the diffraction profiles in SANS and the dependence of domain spacing on the volume fraction of styrene homopolymer, it is found that the homopolymers are isolated in the middle of the polystyrene domain, though they are less concentrated in the middle than the end-parts of the block chains.

Molecular Weight Dependence of Lamellar Domain Spacing of ABC Triblock Copolymers and Their Chain Conformations in Lamellar Domains: The molecular weight dependence of the lamellar domain spacing of isoprene-styrene-2-vinylpyridine triblock copolymers in bulk was studied over the molecular weight range from 40k to 280k by small-angle X-ray scattering (SAXS). It was found that the lamellar domain spacings of the triblock copolymers are larger than those of styrene-2-vinylpyridine diblock copolymers with the same molecular volumes. This result can be interpreted by theories of microphase separation at the strong segregation limit, taking into account the fact that the number of boundaries in the repeating structure of triblock copolymers is twice that of diblock copolymers. Moreover, small-angle neutron scattering (SANS) studies imply that the middle block chain of triblock copolymers is contracted along the direction parallel to lamellae in almost the same manner as the block chain of the diblock copolymers.

Compatibilization Effects of Block Copolymers on Polymer Blends:
SANS experiments have been initiated to examine the effect of block copolymers on the phase behavior of a two component polymer blend. Prior studies have examined the effect of a single homopolymer on the morphology of a microphase separated block copolymer. Studies involving two different homopolymers plus a block copolymer are rare. The model system selected for study was deuterated polystyrene and polybutadiene for the two homopolymers and styrene/butadiene block copolymer. The phase diagram for the two homopolymers without the block copolymer were obtained. Current work involves the addition of varying amounts of block copolymer to the blend of homopolymers, maintaining the ratio of the two homopolymers. This work is the foundation for future studies on the model system to be studied by the Polymer Blends Consortium.

Conformational Analysis of Cyclic Oligomers: The thermodynamics of mixing are shown to be quite sensitive to changes in the topology of blend components. Cyclic bisphenol A carbonate cyclic oligomers [BPACY] are miscible with a wider range of polystyrene molecular weights than their chemically equivalent linear oligomers. This has been explained in terms of a topology dependent Flory-Huggins interaction parameter, with

$$X_{(PS_{Linear}/PC_{Cyclic})} < X_{(PS_{Linear}/PC_{Linear})}$$

This topological dependence has been attributed to conformational restrictions unique to homogeneous cyclic melts. The implication of this interpretation is that the radius of gyration of cyclic oligomers in a homogeneous cyclic melt is smaller than it would be in a chemically equivalent linear oligomer melt. Small angle neutron scattering studies are underway to test this hypothesis.

Molecular Composites Through Hydrogen Bonding: Rod-like Polymers in Blends: The phase behavior and resultant morphology of a molecular composite formed through the blending of a rod-like polymer with a hydrogen bonding coiled polymer has been investigated. The miscibility of a blend of a random copolymer of polystyrene and 1.5% (1,1,1,3,3,3-hexafluoro-2-hydroxyisopropyl) α-methylstyrene (PS(OH)) with poly(hydroxypropyl L-glutamine) (PHOPG) has been investigated. DSC, light scattering and optical microscopy were used to determine the temperature and concentration dependence of the phase behavior and morphology of this blend. The results indicated that this system has a lower critical solution temperature, with a miscible region accessible for $\phi \leq 10\%$, a compositional dependent glass transition, and an ordering of the polypeptide at $138°C<T<153°C$. DSC results suggest that this temperature range ($138°C<T< 153°C$) is where the mobility of the two polymers allows the crystallization of the polypeptide and affects the phase behavior of the blend. Microscopy also suggests a change in the phase decomposition process from nucleation and growth to spinodal decomposition for the 50/50 blend with increased temperature. Future studies will concentrate on examining the effect of shear on this mixture using shear small angle light scattering, verifying the change in the phase decomposition process of the 50/50 sample using light scattering, and extending this study to other rod-like polymers.

Small Angle Neutron Scattering from Dilute Blends of Deuterated Polystyrene in Poly(vinylmethylether) and Protonated Polystyrene

Small angle neutron scattering has been used to study the radius of gyration and thermodynamics of dilute blends of deuterated polystyrene (PSD) in a strongly interacting matrix of poly(vinylmethylether)(PVME) and in a weakly interacting matrix of protonated polystyrene (PSH). The PSD chain is found to be slightly expanded in the PVME matrix over the PSH matrix with the statistical segment length for PSD being 7.3Å in PVME versus 6.8Å in PSH. The Flory interaction parameter, χ/v_o, for the PSD/PVME blend is found to be in approximate agreement with an extrapolation of data from studies of χ/v_o for PSD/PVME at high concentration to the dilute concentrations studied in this work. The concentration dependence of χ/v_o is close to linear and shows no strong change in slope down to $\phi=0.02$, the lowest concentration studied in this work. Analysis of the temperature dependence of χ/v_o and the second virial coefficient, A_2 indicates that phase separation should occur for PSD/PVME in the range of 200°C for a sample with $\phi_{PSD}\sim5\%$.

Small Angle Neutron Scattering of Independently Crosslinked Blends of Deuterated Polystyrene and Poly(vinylmethylether): Blends of polystyrene (PSD) and poly(vinylmethylether) (PVME) have been synthesized where the PVME is crosslinked by an electron beam in the presence of isopropanol (50% concentration). Then the isopropanol is replaced by deuterated styrene monomer and divinylbenzene which is polymerized. This forms a second PSD network which is crosslinked independent of the PVME network. By producing samples by this method it may be possible to synthesize independently crosslinked blends which are thermodynamically miscible. Previous attempts at producing independently crosslinked blends of PVME and PS have resulted in phase separated blends, even in the temperature range where the uncrosslinked blend is single phase. This is due to the loss of entropy from the crosslinking reaction and elastic energy contributions from the swollen network driving the system into the two phase region.

Small Angle Neutron Scattering Studies of Dendrimer Solutions: Dendrimer molecules are polymers formed by a stepwise synthesis in which each additional layer doubles the terminal functionality causing a highly branched and densely packed structure. Work was done in collaboration with Donald Tomalia of Michigan Molecular Institute, who supplied polyamidoamine dendrimers of various sizes. Dendrimers were obtained of ninth and tenth generations having molecular weights of 3.5×10^5 and 7.0×10^5, respectively.

Single chain scattering was measured by extrapolation to zero concentration and both of these dendrimers showed higher order features. Such features have been seen previously in scattering from small objects such as latex spheres, but have not been seen in dissolved single molecules before. This indicates that these large dendrimers are quite uniform.

The size and location of the higher order features are similar to that of either a sphere of uniform density with an abrupt transition at the outside or a distribution that has a maximum segment density away from the center and a zone of transition at the outside.

2. Kinetics of Phase Separation

SANS Studies of Space-Time Organization of Structure in Polymer Blends: Self-organization of structure in polymer blends via spinodal decomposition (SD) was studied over a wide spatial-scale and time-scale (both covering over 4 orders of magnitude) by using a combined time-resolved small-angle neutron scattering and light scattering method. The system studied was a binary critical fluid of deuterated polybutadiene and protonated polyisoprene having a narrow molecular weight distribution in a weak segregation limit. The scattering analyses made it possible to study the space-time organization of various elements of the structure: (i) the global structure, (ii) the interfacial structure such as the mean curvature of the tangled interface, the interfacial area density, and the interfacial thickness, (iii) the "interphase", i.e., the interfacial region with characteristic thermal concentration fluctuations, and (iv) the local structure characterized by the thermal concentration fluctuations within each domain. In the late stage SD, the form factor from the "interphase" was found to be time-independent, having the q-dependence of $q^{-2.5}$.

Effect of Initial Thermal Fluctuations on the Time-Resolved SANS Study of the Self-Assembly Processes of DPB/HPB Blends: Time-resolved small-angle neutron scattering (SANS) experiments have been performed on the self-assembling process of a mixture of deuterated polybutadiene (DPB) and protonated polybutadiene (HPB) at the critical composition. The mixture has an upper critical solution temperature (UCST) type phase diagram with the spinodal temperature at 99.2°C. Specimens held in the single-phase state (at $T=T_i$) were quenched to a point inside the spinodal phase boundary (at $T=T_f$) to induce phase separation via spinodal decomposition (SD). In order to examine the effect that thermal concentration fluctuations present in the single-phase region have on SD, three different $T_i=102.3$, 123.9, and 171.6°C were chosen while T_f was fixed at -7.5°C. The time-dependent SANS structure factor, $S(q,t;T_f)$, showed clear scattering peaks corresponding to the early and intermediate stages of SD. The time changes in the wavenumber $q_m(t;T_f)$ and the intensity $S_m(t;T_f)$ at the peak of $S(q,t:T_f)$ followed different paths depending on the sample temperature before quenching. This fact evidences a definite effect of thermal concentration fluctuations on SD (i.e., a significant "memory" effect). A critical test of the linearized Cahn-Hilliard-Cook theory led to the conclusion that this theory can describe satisfactorily the early stage SD in the deep-quench region.

3. Effect of Flow Field

Shear-Induced Morphological Structures in Triblock Copolymers:

In-situ measurements of the small angle neutron scattering behavior of a styrene-butadiene-styrene triblock copolymer in a steady shear field were made as a function of shear rate and temperature. The kinetics of the scattering behavior after cessation of shear were also examined. In the quiescent state, before shear, an isotropic scattering pattern (in the x-z plane) was observed due to randomly oriented grains of a rodlike microstructure. At low shear rates, the scattering becomes anisotropic, with a set of peaks observed at low scattering angle, normal to flow (z-direction). Above a critical shear rate, a second set of peaks appeared at a higher scattering angle. The peak positions appeared to be consistent with reflections from the 100 and 110 Bragg planes of a hexagonally packed cylindrical array, however a more detailed analysis indicated the two sets of peaks were related to two different structures. Upon cessation of shear, the rate of change in the azimuthal broadening of the first set of peaks was faster than the broadening of the second set of peaks. The ratio of intensities of the two sets of peaks also varied. Two possibilities for the new state that are consistent with the scattering results have been proposed. A TEM study was undertaken to distinguish between these two models. TEM on samples quenched after shear flow shows two distinct types of grains, with different sizes and packing of cylinders. The morphology of this specimen, made at 0.585 s^{-1} and 100°C in the "side-view" and "end-view" conditions, confirms that the primary structure is a hexagonally packed array of cylinders, with an approximate 100 Bragg plane spacing, $d_{100} = 22 \pm 3$nm. A preferred orientation of cylinders is seen, with the 110 planes parallel to the xy-plane of the shear gradient. A secondary structure of small cylinders is also evident, with approximate 100 Bragg plane spacings of $d_{100} = 12 \pm 2$ nm. This second structure is oriented with the 100 planes parallel to the xy-plane of the shear gradient. This constitutes the first direct image of a new morphology excited by shear and the first observation of two morphologies of this type coexisting.

SANS Behavior of Polystyrene/DOP Solutions at High Shear Rates:

A careful examination of SANS data obtained on mixtures of deuterated and protonated polystyrenes in dioctyl phthalate was conducted. In the direction parallel to flow, the scattering at low q is depressed at low shear rates, relative to the quiescent scattering, then becomes enhanced at higher shear rates. In contrast, the scattering normal to flow remains fairly constant at low shear rates, then becomes enhanced at higher shear rates.

The near-isotropic increase in the scattering intensity at high shear rates is thought to reflect a true shift in the critical temperature instead of an effect due to deformation of concentration fluctuations. Values of the critical temperature, T_c, were obtained as a function of shear rate. The data may be fit to a power law which is different than what has been previously observed in other systems.

To obtain a clearer representation of the degree of anisotropy in the scattering, the quantity, $1/S_{\parallel}(q) - 1/S_{\perp}(q)$, was examined where $S_{\parallel}(q)$ and $S_{\perp}(q)$ are the sector averaged structure factors parallel and normal to flow, respectively. From the predictions of Onuki and Kawasaki, $1/S_\parallel(q) - 1/S_\perp(q)$ should scale as $q^{2/5}$ as q approaches zero. The limiting slopes of $1/S_\parallel(q) - 1/S_\perp(q)$ plotted versus q scale as q^σ, where the exponent, σ, is a function of shear rate. The value of σ appears to vary between the mode coupling value of 2/5 and 2. The shear rate dependence of σ may be fit to the empirical relation:

$$\sigma = 2/5 + 8/5[\dot{\gamma}\tau/(1 + \dot{\gamma}\tau)]$$

where τ is a characteristic relaxation time.

For the direction normal to flow, $S(q, \dot{\gamma}=0) - S_\perp(q, \dot{\gamma})$ is invariant for lengths greater than $1/q^*$. This result is in contrast to prior results obtained on high molecular weight polymer blends, where $q^* \propto \dot{\gamma}^{1/3}$. The observed length scale compares favorably to the so-called Debye length, λ_D, for the polymer molecular weight of our solutions. Using this length and the Stokes relation, a characteristic relaxation time can be calculated, which is consistent with our results.

Response of a Liquid Crystalline Polymer to Shear as Studied by Neutron Scattering: The in-situ scattering profile and rheology of a liquid crystalline polymer under shear flow has been measured at various temperatures and shear rates. A 21 wt% solution of poly(γ-benzyl L-glutamate) (PBLG) in deuterated benzyl alcohol (DBA) was sheared at shear rates ranging from 0.07 s^{-1} to 90 s^{-1} at 55°C, 65°C, and 75°C. The neutron scattering pattern was collected at λ=5Å and 9Å to view the sample on different length scales. Viscosity results demonstrate the shear rate regime that was studied includes the plateau and shear thinning regions (regions II and III in the Asada and Onugi scheme). 55°C is near the gelation temperature of this system and results demonstrate that at low shear ($\dot{\gamma} < 0.03$ s^{-1}) there is an alignment perpendicular to the flow for this temperature. This may be explained by the theoretically predicted mechanism of "log rolling". Further analysis has allowed the correlation of molecular response (alignment) to the shear flow and macroscopic response. It was determined that three regimes exist. At low shear rates, there is a gradual increase of the alignment of the molecule by the shear field. At intermediate shear rates, the molecule is generally aligned by the shear with no shear rate dependence on its alignment. Within this regime, the viscosity is Newtonian. At higher shear rates, there is an increase in molecular alignment similar to what is observed at low shear rates. This is also the regime where shear thinning is observed in the viscosity. The transition between these three regimes has been correlated to the first two relaxation times of a rodlike polymer in concentrated solution.

4. Interfacial Characterization, Modification and Phase Separation with Reaction

Structural Stabilization of Phase Separating PC/Polyester Blends Through Interfacial Modification by Transesterification Reaction: Competition between phase separation and transesterification in immiscible polymer blends of polycarbonate (PC) and a co-polyester (PET) was studied as a function of time and temperature by DSC and small angle neutron scattering (SANS). The studies showed the following. 1) Global structure coarsens at T≤

200°C due to the dominance of phase separation over transesterification and melts at T ≥ 220°C due to the dominance of transesterification at the domain interface. However, transesterification is slow but still significant even at T ≤ 200°C. 2) An intricate balance of transesterification and phase separation rates controls global and interfacial structures. 3) Interfacial structures become measurable under certain conditions, and the interfacial thickness between PC or PET and the copolymers generated by transesterification increases with time. 4) DSC results are consistent with results obtained by SANS, but the latter is more sensitive than the former and differentiates the structural changes at different length scales caused by phase separation and transesterification.

Phase Separation and Surface Segregation in Binary Polymer Thin Film Blends: The phase coexistence of polymer blends in thin films can deviate significantly from that in the bulk due to the surface segregation of one of the blend components. Thus, it has been suggested that the presence of the surface may stabilize the phase separated regime in 2-d, leading to a downward shift of the critical temperature. Previous studies on surface segregation showed that enthalpic factors usually dominate the segregation of blend components to different surfaces. However, many subtle factors such as chain length and statistical segment length can also play significant roles. Neutron and x-ray reflectivity were used to follow the thin film phase separation in the deuterated polystyrene/poly(vinyl methyl ether), dPS/PVME, system. Experiments were conducted at different compositions, temperatures and film thicknesses in an effort to map the thin film phase diagram of this classic LCST blend system.

Chain Ends and Junction Point Distributions in Ordered Block Copolymer Thin Films: Lamellar ordering in nearly symmetric PS-P2VP block copolymers were examined by neutron reflectivity in a thin film geometry. The PS blocks were selectively deuterated at the junction points or at the chain ends to determine their spatial distribution within the lamellar domains. The reflectivity analysis showed the PS-P2VP interface to be extremely narrow (~25Å), with the junction points confined to the interfacial region. In contrast, the chain ends exhibit a broader maximum in the center of the domains. The molecular weight dependence of the chain end and junction point distributions, and compatabilizing effects with homopolymers are being investigated.

Silica Filled In-Situ Composites: Organic-inorganic interpenetrating networks were synthesized and characterized in an effort to make silica filled polymeric materials. The samples were made by forming SiO_2 by hydrolysis of tetraethylorthosilicate and by forming organic polymer by the free radical polymerization of 2-hydroxyethyl acrylate. No solvent was necessary, but the loss of the hydrolysis product, ethanol, caused some shrinkage. Hydrogen fluoride and benzoyl peroxide were used to catalyze the inorganic and organic polymerizations respectively, and samples were made with a range of relative rates of polymerization of the two components.

Small angle neutron scattering, small angle x-ray scattering, and transmission electron microscopy were used to characterize the resultant morphology. When the vinyl polymerization was more rapid than the sol-gel reaction, macroscopic phase separation occurred producing a very heterogeneous sample. When the sol-gel polymerization occurred first, a very uniform two phase morphology resulted with a characteristic size less than 10 nm. At relative rates between these two extremes, dendritic structures resulted. Small angle scattering results were consistent with microscopy, giving power law scattering for the dendritic structures.

5. Sensor Development for Characterization and Process Monitoring

Fluorescence Anisotropy Measurements: This measurement involves the use of polarized light to determine the anisotropy of a fluorescent dye molecule which has been doped into a polymer matrix at low concentrations. An essential requirement for anisotropy sensitivity to shear stress is that the probe molecule engage in the entanglement network of the matrix polymer, i.e. it must be macromolecular in size. Thus, under shear stress, the anthracene tagged polybutadiene probe showed significant change with shear stress, but small fluorescent probe molecules, which are unable to engage in the molecular entanglement network of the matrix, are insensitive to shear stress.

For extension, we have observed that the entanglement requirement does not apply. This is probably because large orientations are possible under extension stress whereas only limited weak orientation occurs under shear stress. Small rod-like fluorescent molecules, such as anthracene and diphenyl hexatriene, which associate their long axis with the polymer main chain extension, display fluorescence anisotropy change with applied extension stress, in contrast to no significant change with shear stress. These observations were carried out using cross-linked polybutadiene and demonstrate that the rod-like probes can be used to detect the presence of extensional stress in mixed extension and shear stress fields.

Optical and Ultrasonics Monitoring of Injection Molding: The objective of this program is to develop new measurement methods for monitoring polymer injection molding processing. Ultrasonics and optical measurements are employed to measure, in real-time, resin flow front velocity, mold filling time, temperature at the injection nozzle, onset of resin solidification in the mold, part shrinkage upon solidification and cooling, and resin modulus. Considerable progress has been made on several of these measurements, e.g. mold filling time and solidification time. The data present a view of resin state changes in the mold cavity during the most critical phase of the mold cycle.

6. Theoretical Studies

Equilibrium Phase Behavior of Blends

Polymer blends exhibit Ising critical behavior near the critical point for phase separation while mean-field type critical behavior is obtained far from the critical point where critical fluctuations are small. There is also an intermediate 'crossover' regime where neither mean-field or Ising type scaling is exhibited. These regimes are precisely prescribed in terms of the Ginzburg number, G_i, calculated from the compressible Flory-Huggins theory. The combination of the Flory-Huggins theory and the renormalization group theory indicates that mean-field theory breaks down for $\tau \geq G_i$ and the critical regime is restricted to the range $\tau \leq G_i/10$ where τ is the reduced temperature $\tau = (T-T_C)/T$ such that $\tau > 0$. The calculations indicate that monomer structure and compressibility have a strong influence on the phase stability of blends (T_C) and the width of the critical regime.

Critical Dynamics of Diluted Blends

The critical dynamics of moderately high molecular weight blends of polystyrene (PS) and polybutadiene (PB) diluted in dioctyl phthalate exhibits features remarkably similar to the melt blend. These observations suggest that the melt blend should be considered as a three component system where vacancies, arising from the inefficiency of chain packing, should be considered the third component. Critical exponents in diluted blends at constant pressure are expected to shift substantially due to Fisher renormalization. Evidence for Fisher renormalization exponents are found for both the diluted (DOP) blend and the melt PS/PB blend. These observations are basic for modelling the phase separation in these blends. The generality of this effect remains to be determined.

Geometrical Properties of Polymers in Dilute Solution

The problem of the characterization of polymers through the measurement of dilute solution properties (radius of gyration, ...) and the comparison of model calculations to experiment remains a basic activity in polymer science. Previous lattice model calculations of dilute polymer configurational properties (SAWS) are extended by using the Suzuki coherent anomaly method. The calculations provide a test case before the methods are applied to problems associated with polymer blend phase separation. We find that there are significant limitations on the 1/d (d is the dimensionality) expansion method in situations where fluctuations are large.

Translational Friction on an Arbitrarily Shaped Brownian Particle

Hydrodynamic measurements are a primary source of polymer molecular parameters (molecular weight, size, shape). These measurements include the translational diffusion coefficient, rotational diffusion coefficient, intrinsic viscosity and the sedimentation coefficient. It is shown that the scalar translational friction of an arbitrarily shaped particle is related to the electrostatic capacity of the same body. This hydrodynamic-electrostatic "analog" allows for the analytical calculation of the translational friction in many new cases (short circular cylinders, cube, ...) and provides fundamental new theoretical insight into the physical origin of friction. A Brownian dynamic algorithm is developed to calculate the capacity (friction) of bodies having shape and the method applied in a number of test cases - cube, intersecting spheres, random and self-avoiding walks with beads positioned at the walk vertices. In all cases the program allows for accurate calculations of the friction where a configurational preaveraging approximation has been made.

Polymer Adsorption and Desorption Kinetics

A theoretical model of polymer adsorption and desorption is developed which stresses the transition from kinetics governed by energetic factors at high temperatures to kinetics dominated by kinetic factors at lower temperatures. The rate of desorption at lower temperatures is modelled by the Smoluchowski rate of diffusion from a plane surface. Combining this estimate of the rate of desorption with kinetic theory leads to a prediction of stretched exponential desorption where the time constant is inversely proportional to the solution diffusion coefficient D. The predicted transition from exponential to stretched exponential desorption kinetics and a desorption time constant scaling inversely with D have been observed in experiments.

NIST /INDUSTRY CONSORTIUM ACTIVITIES

C. C. Han, A. J. Bur, E. A. Di Marzio and F. W. Wang

New Measurement Technology for Polymer Processing Consortium

This consortium is an outgrowth of an NIST/Industry workshop which was held at NIST in December, 1990. The objectives of the workshop were: (a) to seek industry responses to the question: what on-line, real-time measurements do you need to make during polymer processing, but are unable to do so because the measurement technology does not exist? and (b) to put together a collaborative NIST /Industry research program for development of new measurement technology. Processors identified their measurement problems by describing various processing operations. Workshop discussions yielded a consensus of the following measurement needs: (a) in-line rheological measurements; (b) improved in-line temperature measurements; and, (c) in-line and on-line measurements of polymer morphology. The direct interaction with industry at this workshop provided the framework for defining the consortium research program which is dedicated to the development of new in-line measurement technology for polymer processing based on optical and fluorescence methods. The consortium research program will extend over a period of four years during which rheology and temperature measurement systems and concepts will be developed.

Polymer Blends Consortium

The objective of this consortium is to understand the variables controlling the mixing/demixing kinetics. These factors are critical to all polymer blends/alloys processes which are designed to control the structure and morphology of the final material and consequently its tailored properties. The relevant scientific areas include: (1) Thermodynamics of polymer blends; (2) Kinetics of phase separation; (3) Effects of crosslinking and grafting on the thermodynamics and kinetics; (4) Shear mixing/demixing and phase separation kinetics after cessation of shear; (5) Interfacial modification and control; (6) Simultaneous reaction and phase separation/structure stabilization. The multivariant model inferred from these studies can be used to guide new product development and hopefully in the future will be used as part of an intelligent processing system for on-line control.

Two workshops were held at NIST in April, 1992 and February, 1993 in order to establish dialogue with potential industrial partners and to solicit input from chemical producers. These led to the first consortium meeting on September 24, 1993. At the time of this meeting, five companies (Rohm and Haas, Raychem, 3M, Armstrong World Industry and Aristech) had formally signed agreements to join the consortium, while another eight companies, one national laboratory and two universities (Lockheed, Allied Signal, Exxon, Goodyear, Sandia National Laboratories, Huron, University of Texas and Stanford University) were in the process of negotiating membership.

The current blends consortium effort will be concentrated on the laboratory experimental measurements for up to three blend systems. Existing SANS, Shear SANS, LS and Shear LS instruments will be made available for consortium projects. The new shear light scattering instrument with video microscope detector will become available to members in the future.

POLYMER COMPOSITES

Polymer composites are light-weight, high-strength materials whose properties can be extensively tailored. By using these advantages, products can be made which have dramatically improved properties and are therefore more competitive in world markets. There are many opportunities to exploit this potential in areas such as infrastructure, electronics, off-shore oil rigs, construction, commercial aerospace, and medical devices. At least in the short term, however, the largest potential market is automotive components. As a result, this is the initial focus of NIST's composite program. Much of the work is generic, however, and thus relevant to many other applications. Where appropriate, these applications are also considered.

Although composites have great potential, the opportunities remain largely unexploited. This can be attributed to two critical barriers that hinder the wider use of these materials: (1) the need to improve the speed, reliability, and cost effectiveness of fabrication, and (2) the need to develop a better understanding and predictive capability for long term performance. The work in the Polymer Division seeks to address both of these challenges with a major program that has tasks on **Processing Science** and **Durability and Aging Behavior**. The Processing Science Task and the durability studies are conducted in the Composites Group while issues in mechanics and aging are addressed in the Structure and Mechanics Group.

The Processing Science Task is concerned with four fabrication methods: advanced autoclave cure, filament placement, press molding, and liquid composite molding (LCM). Most work, however, centers on LCM, which includes resin transfer molding (RTM) and structural reaction injection molding (SRIM). This emphasis is based on the advice of industry obtained through a variety of mechanisms, including NIST sponsored Industry Workshops. LCM is also the choice of the automotive industry for manufacture of structural composite parts. The consensus is that LCM offers the best possibility to achieve fast, reliable, and cost effective composite production. The work on durability is new, but it builds on strong programs at NIST on the mechanics of composite resins, including work on viscoelastic properties, physical aging, and toughening. Based on the advice of industry, the initial effort on durability is a study of environmental attack on composites; i.e., the effects of moisture, loads, and temperature on composite performance. A key element in the work is an emphasis on identifying and quantifying the mechanisms of degradation. Because these questions are critical to a wide range of applications, the effort in this area is expected to grow, particularly as interest in infrastructure applications builds.

During the past year, work in the Composites Group has been enhanced by interactions with many outside organizations. In the area of processing science, the cooperating groups include the Automotive Composites Consortium (Ford, General Motors, and Chrysler), General Electric, Ford, Grumman, ViGYAN, Boeing, Johns Hopkins University, the University of Delaware, and North Carolina A & T. Organizations cooperating with the durability work are the Automotive Composites Consortium, Dow Chemical Company, Owens Corning, Exxon, and Grumman. The group staff changed considerably during the year. Dr. S. S. Chang retired after many years of contributing to the composites programs, and Dr. W. Wu moved to the Electronic Applications Group. Dr. Wu's work in interface characterization remains very relevant to the composites effort, however. Joining the group were Drs. C. Schutte and C. Schultheisz who bring expertise in composite testing and durability. Finally, Ms. K. Flynn was hired to assist the LCM program. Dr. S. Ranganathan who has a postdoctoral position at the University of Delaware is spending a year working at NIST in the process simulation area. Dr. M. Shioya from Tokyo Institute of Technology completed his sabbatical at NIST working on the fiber-matrix interface and Dr. C. Moon from Pusan National Fisheries University in Korea is beginning a sabbatical. Dr. Y. Tirosh from Technion Institute of Technology in Israel completed a 3 month sabbatical working on mechanics of toughened materials. Finally, Mrs. D. Woerdeman continues to work in the composites program to complete her research work for a PhD at Johns Hopkins University.

The discussion below begins with a list of major accomplishments in the Composites Group, and then proceeds with four sections describing the activities during the past year. The first section is a short summary of the results from a Workshop on LCM sponsored by NIST. The next two sections cover the Processing Science and Durability Tasks in the Group. The final section discusses activities which draw upon expertise in the Group but are outside the Task areas.

FY 93 Significant Accomplishments

- In cooperation with the Automotive Composites Consortium, a design was developed to instrument a mold for fabrication of a structural automotive part, the cross member in a van. This part is very complex so the mold provides an excellent tool to investigate structural reaction injection molding, and to test the Division's process simulation models. Previous work in this cooperative program has used these simulation models to describe mold filling for other structural automotive parts.

- While conducting permeability measurements for the Automotive Composites Consortium, a material with the principal axes of the permeability tensor tilted out of the plane of the fabric was discovered. Until now, this possibility has not been seriously considered, and thus the current measurement procedures cannot characterize the permeability of such a material. We believe that many more examples of this behavior will be found as more complex preforms are constructed. To address this problem, a new software analysis package has been developed and appropriate experimental equipment and methods are currently being designed.

- A new standard reference material (SRM) package has been developed for permeability of the fiber preforms used for liquid composite molding. This SRM was produced at the request of industry and consists of two samples: a random mat material and a 3-dimensionally woven fabric. The SRM is now undergoing round robin testing.

- A workshop of industry, university, and government experts in liquid composites molding (LCM) was organized and hosted by NIST. The attendees identified critical challenges that must be addressed to improve the LCM processing method, and these will be used to help plan future directions in the NIST program.

- Moisture-exposure experiments conducted on single-fiber fragmentation specimens of E-glass/epoxy show that the water attacks both the fiber and the fiber-matrix interface. Evidence supporting fiber degradation includes the detection of ions from the fiber in the immersion water. This suggests the complexity of the degradation problem and illustrates the need for systematic studies.

- A new analysis has been developed which allows both the fiber and interface strengths to be estimated from each experiment in the single-fiber fragmentation test. The fiber strength is needed to estimate the interface strength from fragmentation results, but the fiber strength is difficult and time consuming to measure independently. Consequently, the new analysis is a major advance, particularly for studies like moisture attack where the water degrades both the fiber and interface strength.

WORKSHOP ON FLOW PROBLEMS IN PROCESSING OF COMPOSITES BY LIQUID MOLDING

An international meeting entitled "Workshop on Manufacturing Polymer Composites by Liquid Molding" was organized by NIST staff and held September 20-22, 1993 at NIST under sponsorship of NIST, General Electric (Andy Salem), and Ford Motor Company (Ken Kendall). Most of the leading experts on liquid molding in the United States as well as a number of international authorities participated. The goals of the Workshop were to clarify the fluid flow issues facing the industry, open lines of communication between those working on each issue, and focus attention on those issues deemed most critical at the present time. The meeting used posters and invited lectures to introduce the major issues and then divided into five discussion groups devoted to defining the critical challenges presented by each major issue. A total of 65 people, predominantly from industry, but also from universities and government, attended the meeting.

The five discussion groups focussed on: (1) model validation and test methods, (2) high speed processing, (3) preform architecture and permeability, (4) reinforcement/resin interactions during flow, and (5) heating and rheokinetic effects during flow. Although the discussions revealed notable disagreement between the academic and industrial communities on priorities for the various issues, there was nearly complete agreement on many of the challenges that most deserved further attention. The challenge deemed most critical is the need to understand and model the deformation process that the fibrous reinforcement undergoes when it is shaped and placed in the mold. This deformation can change the flow pattern and permeability tensor in ways that must be predictable. Two other issues also considered essential to the progress of the liquid molding industry are: the establishment of standard materials and procedures for permeability measurements and the development of a data base for permeability and related processing information. Another concern for many industry representatives was the issues of high speed processing and how rapid fluid flow might cause preform deformation in the mold. A more complete description of the conference and its conclusions will be available as a NISTIR.

PROCESSING SCIENCE - LIQUID COMPOSITE MOLDING

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As indicated previously, the primary focus in the Processing Science Task is Liquid Composite Molding (LCM). Effective use of LCM requires further developments in both preform fabrication methods and the technology required for process optimization and on-line process control. Preform suppliers and others have large efforts in preform fabrication technology. To complement these efforts, the National Institute of Standards and Technology (NIST) has initiated a major program to address the scientific issues associated with process optimization and control.

The projects in this program generally follow four steps. The first step is to characterize the starting materials for processing related properties. Two features of particular interest are the permeability and microstructure of the fiber preform. The second step is the development and utilization of process simulation models. These computer programs fall into two categories. The first is termed macro-models since the programs treat macroscopic behavior by averaging microstructural details over some finite volume to simplify the information needed for the analysis. These models are ideal for global events such as mold filling, but are generally inadequate for describing events, such as void formation, that depend on local structure. As a result, the work also develops micro-models to address questions like the prediction of permeability from a knowledge of microstructure. Although this is a long range goal, the potential pay off is great. The third step in the processing science projects is the development and application of process monitoring. The objective is to generate feedback on the validity of the predictions from the process simulation models so they can be refined and improved. In addition, the work helps to provide the technology needed for on-line process control. The measurement methods range from simple flow visualization to sophisticated fiber-optic techniques. The final step in many projects is the use of the technology developed to make test samples and, with the assistance of industry, full scale parts. This provides tests of the validity of the NIST results, as well as an ideal way to transfer the technology to industry.

During the past year, the work has involved projects in five areas. First, there was the development of new facilities for the processing laboratory and for on-line process monitoring. Three other projects related to permeability. One focused on standards with the development of an SRM and the initiation of work on a data base; another project concerned the measurement of permeability and an evaluation of the approximations often used in such measurements, and a third permeability project focused on prediction methods. The final area of research in Processing Science involved efforts to refine and verify the process simulation models for macroscopic mold filling. Each of these five projects is reviewed below.

Permeability and Process Monitoring Facilities

During the past year there have been some important upgrades and new acquisitions to the processing facilities. The permeability measurement laboratory was automated through the development of an integrated software package for configuration and control of experiments, and acquisition and analysis of data. The software was written in Visual Basic to present a graphical user interface that can be easily learned by the many students and visitors who use the facility. In addition, an image processing system has been purchased to automate the analysis of video data accumulated during flow visualization experiments.

The major effort, however, has been in the area of process monitoring. Over the years, NIST has built-up extensive expertise and facilities in the area of process monitoring including capabilities for all of the common monitoring techniques. From this collection, a small number of methods have now been chosen for development in the LCM program. The initial research effort is using optical-fiber evanescent-wave fluorescence experiments in an attempt to develop a single sensor for both flow and cure monitoring. Fluorescence has been shown to provide accurate cure monitoring data at NIST and elsewhere, but this capability has not been applied to liquid molding. To accelerate this ongoing effort, a new staff member will be joining the Division next year.

An optical bench and heated mold were built to perform the fluorescence experiments. The bench is designed to focus a 488 nm wavelength laser beam into an optical fiber and detect a fluorescence signal exiting from the fiber at wavelengths above 500 nm. Although the exciting beam is totally internally reflected through the optical fiber, a standing wave exists on the outer surface of the fiber at the excitation wavelength. This standing wave can interact with the surrounding material and, in this case, cause the resin system to fluoresce. A portion of the fluorescent radiation couples back into the fiber and propagates to the detector. At this time, evanescent wave fluorescence has been demonstrated with this optical bench, and the optical equipment is being calibrated for the cure monitoring experiments.

The heated mold was designed to permit the entrance and exit of optical fibers as well as to provide heat to the internal cavity. The mold is electrically heated, and a feedback temperature control loop allows for programmable cure cycles through computer control. Optical fibers are introduced to the mold through any of 10 special ports in the side walls of the mold. To date, a small number of parts have been fabricated to prepare for integrating the injection and optical systems.

Permeability Standards

Perhaps the single most critical material property for understanding and predicting processing in LCM is the permeability of the fiber preform. As indicated in the Liquid Molding Workshop, however, the measurement of permeability is a major problem for industry, and a strong recommendation was given for the establishment of standards and a data base of information. Efforts in both of these areas have been underway at NIST for more than a year, and a Standard Reference Material (SRM) package for permeability is now ready for round robin testing. The package will contain 2 samples: a simple material for developing the measurement techniques, and a certified sample for quantitative comparison. The latter is a 3-dimensional woven glass fabric of 52.5% nominal fiber volume fraction. The 3-D woven material was chosen over the traditional 2-D woven or unidirectional materials to reduce material handling errors. 3-D braided material could not be used because of extreme cost.

A summary of the qualification experiments for the woven glass fabric is illustrated in Figure 1. Figure 1a shows the magnitude of the in-plane permeability tensor **K** measured in a saturated, steady-state unidirectional flow experiment at the indicated angle relative to the fill fiber direction. The experiments were conducted at flow orientations of 45° and 135°, and yielded the same permeabilities. This is expected based on the results presented below which indicate symmetry about the fill fiber direction in the fabric. The triangular symbols in Figure 1a illustrate the range of data obtained for **K** using flawless samples of the 3-D woven material randomly selected from the SRM packages. Despite careful sample preparation, the fiber volume fraction of the SRM material may vary by as much as 0.5%, and the value of **K** varies accordingly. The permeability of this material will therefore be defined over a range of fiber volume fractions in the certification as an SRM. Additional data, presented in Figure 1a as circular symbols, represent measurements on samples not subjected to the quality control checks applied to the material included in the SRM packages. Clearly quality control is very important.

Figure 1b shows the flow front position as a function of time in a transient radial flow experiment. These results indicate the geometry (directions of maximum and minimum flow) for the in-plane permeability tensor **K**. As can be seen, the major axis of **K** is oriented along the fill fibers, and the ratio of the principal components of **K** equals approximately 1.75. Several radial flow experiments were conducted with results reproducible within 3% for these values. Moreover, an analysis of the unidirectional experiments gives values for the geometry of **K** that are perfectly consistent with what is seen in the radial flow

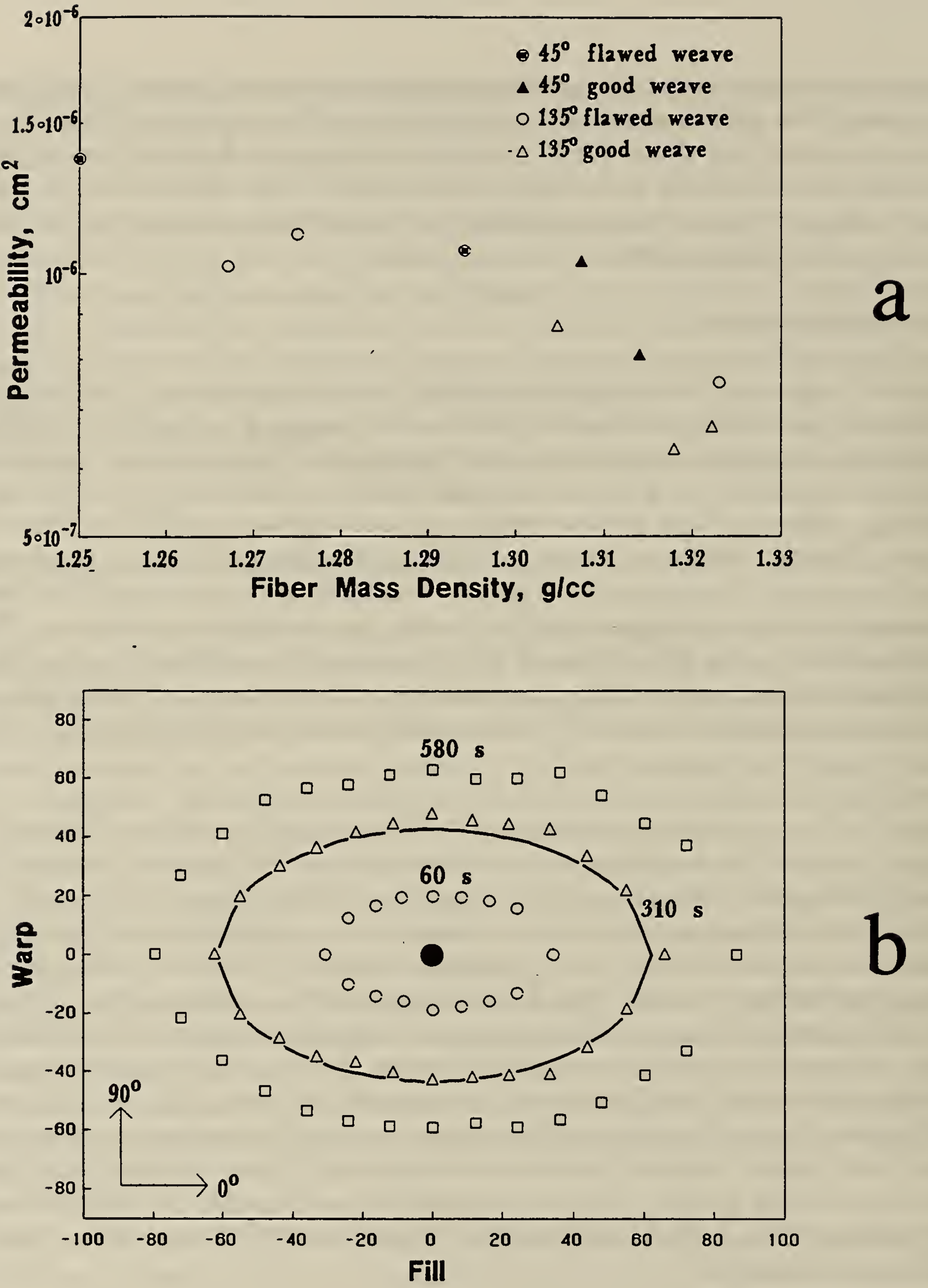


Figure 1: Flow data for the 3D woven SRM. The effective permeability in unidirectional flow measured with 45 degrees or 135 degrees between the flow direction and the fill fiber direction in the fabric are plotted as a function of fiber mass density (a). The fiber volume fraction is approximately equal to the fiber mass density divided by 2.5 so the corresponding fiber volume fraction range is 0.5 to 0.53. The flow front position is shown in (b) at the 3 indicated times for a radial flow experiment with injection rate of 0.2 ml/s.

experiments. As expected, a quantitative analysis of the radial flow experiments gave values for the magnitude of **K** that were not consistent with those found in the unidirectional experiments. This discrepancy between transient and steady-state saturated flow behaviors is well known and has been attributed to the heterogeneities in the fabric microstructure.

An outgrowth of the SRM project is a new program designed to establish a data base in this area. In addition to the permeability data accumulated for the SRM material, the laboratory has also measured the permeability of a variety of reinforcement materials for our industrial collaborators which include the Automotive Composites Consortium (ACC), the GE/Ford ATP partnership, GEAir, Boeing, DOW, and Grumman. These data, along with reliable data from other facilities, will be entered into a data base under development by the Standard Reference Data Program at NIST.

Evaluation of Experimental Permeability Characterization

Accurate permeability data are a critical requirement if flow simulations are to be successfully used in the design and optimization of LCM processes. Currently, determination of the permeability tensor is best accomplished through experimental measurements, and a variety of methods involving flow in 1D, 2D and 3D molds are used. In all of the methods, the extraction of permeability values from the experimental measurements involves the use of approximate solutions when the material being measured is anisotropic (i.e. the principal components of the permeability tensor are not equal). During the past year, flows in the different types of molds commonly used to measure permeability were analyzed using NIST's FEM code, RTMFill. These calculations were undertaken to check the magnitude of the error introduced by the use of approximate solutions to analyze the data.

One and Two Dimensional Considerations: For the case of a 1D measurement technique, the critical assumption used in analyzing the data is that the velocity components perpendicular to the main flow are zero. At the inlet and outlet end of the mold, this condition cannot be satisfied due to the constraint of constant pressure across the boundary. As a result, the positions selected for the pressure taps used in the measurement become important. The finite element solution for flow in this geometry was used to calculate the effective permeabilities that would be measured for pressure taps placed at different locations in the mold. An experimentally determined permeability tensor was used for the analysis. It was assumed that the direction of maximum permeability in the preform was oriented at an angle of 45 degrees to the flow direction and the anisotropy was 0.61. If the pressure taps are at the inlet and outlet points, the results show that the influence of the inlet and outlet boundaries approximately cancels out and introduces an error of only 5%. Calculations performed for more highly anisotropic materials show, however, that the error becomes larger with increasing preform anisotropy and is maximized at the 45 degree orientation. Fortunately, for most woven materials in common use, the anisotropy is low enough that the errors involved are small.

Flow in 2D permeability molds was also analyzed. Error is introduced in the experiments with anisotropic materials because the inlet to the mold is generally circular, while the flow front will evolve to be elliptical. The experimental analysis is based on the assumption of an elliptically shaped flow front for all times which means that the inlet must also have this shape. As might be expected, the calculations show that the influence of the gate becomes negligible once the overall dimensions of the elliptical flow front are much larger than the gate diameter.

Three Dimensional Considerations: The situation becomes much more complicated when 3D considerations are involved. The 3D information is important because LCM is particularly well suited to the generation of large, complex parts where 3D flows during processing are inevitable. Moreover, modern preforms are often made by combining layers of materials with widely varying permeability. Under these conditions, the flow can race through the high permeability layer and then penetrate through the thickness into the lower permeability layer. Finally, the 3-dimensional nature of modern preform architectures raises an additional issue. All current measurement techniques assume that a principle axis of the permeability tensor lies in the plane of the fabric. Although this is probably a reasonable assumption for simple materials, it may not true for 3D fabrics or layered preforms. Until now, however, no serious consideration has been given to this possibility. During the past year, permeability measurements were conducted for the Automotive Composites Consortium on a layered, unidirectional material of particular interest to them. The results clearly show that the principal axes of the permeability tensor are tilted out of the plane of the fabric. Although the material does contain stitching threads in the third direction, the structure does not seem to be particularly complex, and thus the results suggest that there may be many materials with this type of permeability. It is essential therefore to develop new measurement procedures and data analysis methods so such materials can be characterized.

To address this question, a general methodology was developed for measuring and interpreting data from a 3D permeability experiment. The protocol relies strictly on unidirectional, saturated-flow experiments since the radial flow experiment is a strictly in-plane measurement and cannot be used to obtain out-of-plane data. For this situation, at least six unidirectional measurements in different orientations are required since a 3-D orthotropic tensor contains 6 unknowns. The experiments involve measuring the effective permeability, k_{eff}, in the six directions and then solving 6 highly nonlinear equations to find the 6 unknown components of the permeability tensor: K_{xx}, K_{yy}, and K_{zz} are the principal permeabilities of the permeability tensor K, and Θ_x, Θ_y, and Θ_z are the orientation angles of K relative to the fabric's coordinate system. An approximate solution for k_{eff} was obtained but is still quite complex. Moreover, to obtain the components of the permeability tensor, the six simultaneous equations for k_{eff} must be inverted, and a computer program for doing this was developed. Because the relationships are so complex, however, it is important to know what errors are introduced by the approximations involved.

To judge these errors, a set of six hypothetical experiments was selected and an assumed permeability tensor was used to predict effective permeabilities for the six experimental situations based on the equation described above. A more exact analysis was then performed using NIST's 3D FEM code, RTMFill, to calculate the effective permeabilities. Both a coarse and a refined mesh were used and the results are shown in Figure 2. As seen in this figure, the agreement was excellent which indicates that the approximate equation provides a useful method to determine 3D permeabilities in complex materials.

Once the 3-D **K** is obtained, 3-D flows can be understood and modeled in realistic preforms such as those which contain layers of differing materials. An experimental study of this situation was initiated last year using multi-layer preform architectures. The results show that 2 or 2.5-D Darcy law based simulations can lead to serious errors by neglecting through-thickness flows. Such errors arise because the permeabilities of the different layers in the preform are averaged inappropriately for unsaturated flows in the standard 2- and 2.5-D models. Moreover, it is unclear how to properly average the permeabilities. Computations using NIST's 3D simulation for such situations are planned for next year.

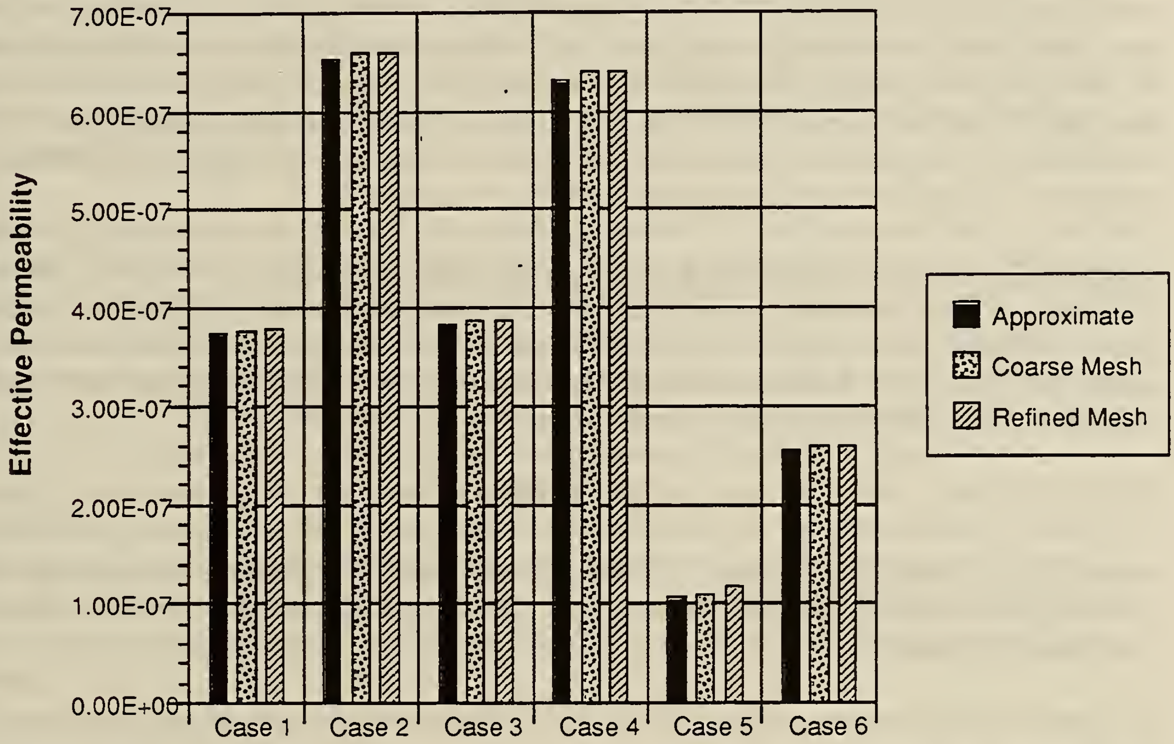


Figure 2: Comparison of effective permeability values calculated using an approximate solution method, and direct determined from finite element solutions for the six different flow cases needed to fully characterize the 3D permeability tensor. The FE solutions were determined for both a course and a fine mesh.

Permeability Prediction

One of the goals in the NIST program is the development of a capability to predict permeability from a knowledge of microstructure. Although this objective is very long term, the potential pay-off is high. Moreover, in the short term these models should make it possible to predict trends, interpolate data, and determine how the deformation of a preform will effect permeability. This last area was identified in the LCM Workshop as very important.

The program uses two model geometries to test the predictions. The first involves unidirectional materials which represent a relatively simple geometry at least in the sense that it is 2D. The second example is the 3D woven material used in the NIST's SRM. This material has a complex microstructure, but will be well characterized for permeability as part of the SRM program.

Past work has demonstrated the sensitivity of the permeability tensor to the preform microstructure and the need for a 3D model to treat anything but the simplest geometries. A major accomplishment during the past year was the development of such a model so next year more complex preform architectures can be addressed. In addition, the simple analysis of unidirectional material was extended from flow parallel to the fibers which was analyzed last year to include flow perpendicular to the fibers. Work was also conducted to develop the technology required to characterize the microstructure in both simple and complex materials. Results for the last two areas are discussed below.

Microanalysis of Flow Transverse to Aligned Porous Fiber Tows: To predict permeability in fibrous media, the model must include not only flow between the fiber tows but also flow inside the tows, since they are bundles of fibers and therefore porous themselves. To accomplish this, flow inside the tows is described using the Brinkman-volume averaged momentum equation (BVAME), which is given by

$$\nabla P = \mu(\nabla^2 \boldsymbol{v} - \boldsymbol{K}^{-1}\boldsymbol{v}) \tag{2}$$

where **v** is average fluid velocity, $\boldsymbol{K}$ is the permeability of the porous tows, μ is the fluid viscosity, and P is the pressure. Flow in the open region between the tows is modeled using the Stokes Equation.

A rigorous finite element analysis of flow in a square array of tows aligned transverse to the flow shows that even for very highly permeable cylinders, most of the pressure drop in the system occurs in the narrow gap between adjacent cylinders. This prompted an approximate analysis based on lubrication theory. The result is a semi-analytical model for the overall bed permeability given by an integral equation. The resulting expression for permeability is a function only of the tow shape, packing characteristics, and intra-tow properties. The integration can easily be performed numerically, and is far less work than carrying out an entire finite element analysis. The model predictions have been verified by comparing with results from rigorous finite element calculations using the commercial FIDAP software package. The model shows that the influence of the intra-tow permeability on the overall bed permeability increases with inter-tow packing, and increasing degree of tow ellipticity. The intra-tow influence is particularly critical for "stacked" geometries where previous models predicted a zero permeability. An important parameter in the expression is the intra-tow permeability. A method for predicting this parameter from the intra-tow fibril diameters and overall tow shape was investigated. Comparison with limited experimental data shows that using this method to predict the intra-tow permeability, and then using this value in the integral equation for permeability, enables good correlation between predicted and measured values.

Microstructural Determination: To compliment the modelling work, studies are underway to develop methods for determining microstructure in a reinforcing fabric. This study is examining the two model systems mentioned above: the 3-D woven SRM, and a unidirectional fabric. Although the unidirectional material would seem to be the simpler of the two, the requirement of stacking many layers to form a laminate of thickness equal to the 3-D woven material led to a number of interesting structural features. In order to immobilize the reinforcement fibers for structural characterization, composite panels were molded with epoxy resin using either two layers of 3-D woven material or 15 layers of unidirectional material. This produced thicknesses of 6.35 mm (0.25") at a fiber volume fraction of approximately 50%. The panels were then sectioned, polished, and examined under an optical microscope.

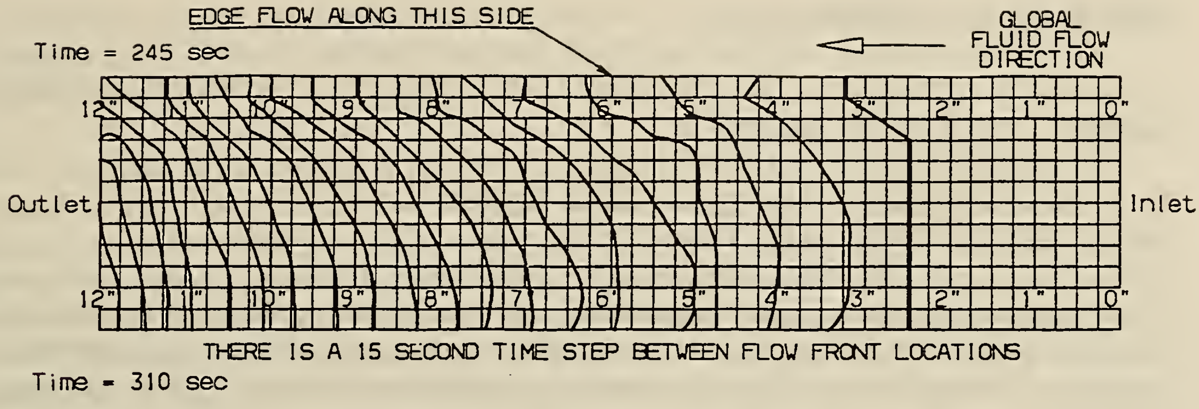
The results of image analysis indicate that idealized models of reinforcement fabric may not be adequate. For example, the fill fibers in the 3-D woven mat executed a wavy shape in space, but the idealized model of the fabric assumed the fill fibers lay flat between layers of warp fibers. Nonlinear least squares curve fitting of the fiber trajectories in the panel indicates that a sinusoidal function can provide an adequate description of the warp and fill fibers, and that the fill fibers undulate with approximately half the amplitude and twice the frequency of the warp fibers. Although the development of the ability to predict the permeability is attractive, the above work raises questions about the relative ease of structural characterization compared to the permeability measurements. If the permeability is highly sensitive to structural irregularities then microstructural characterization may prove very difficult compared to permeability measurements. It may be useful to conduct sensitivity analysis with the predictive models to determine which structural parameters are most important.

Macro-Flow Model Verification

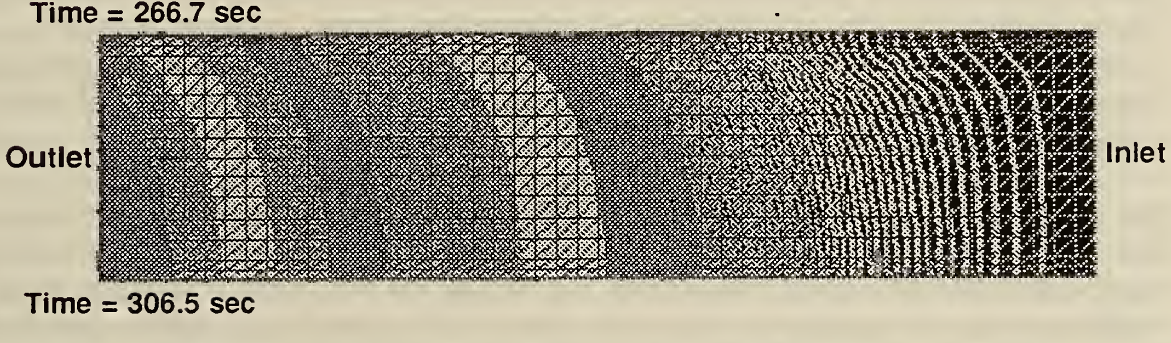
A major challenge in the Processing Science Task is verification of the process simulation models. There are both in-house and external collaborations addressing this question. The external interactions involve a number of organizations including the Automotive Composites Consortium (ACC). The ACC cooperation was described in detail last year, and so it will not be discussed here except to summarize an important accomplishment related to the preparations for a new study. The plan is to fabricate a series of cross-members for a van by LCM and compare the results with predictions from the Division's process simulation models. This part is a very complex and therefore provides an excellent tool to study the LCM process and test process simulation models. In preparation for this work, detailed discussions have been held with the ACC to determine the best positions for placement of pressure sensors in the mold. Preliminary computer simulations were performed to determine the most critical areas of flow in the mold, and the ACC's knowledge of the mold construction provided insight into where sensors could be placed without major disruptions to the mold. Modification of the mold to add sensors is now underway and fabrication experiments are planned for next year.

Another industry interaction is a program initiated in 1991 with Grumman Corporation (R. Leek, G. Carpenter, A. Rubel, and T. Donnellan). In this collaboration, NIST provided its mold filling program, RTMFill, and Grumman provides feedback on the predictive capabilities of the code through flow visualization experiments. Last year, Grumman conducted a series of experiments using "edge flow" geometries. These studies involved a 7.62 cm (3 in.) wide by 30.48 cm (12 in.) long by 0.432 cm (0.17 in.) thick flat plaque geometry. Fluid was injected along one of the 7.62 cm wide edges at a constant inlet pressure of 1.38 x 10^5 Pa (20 psi). The mold was filled with 15 layers of style 1564 fiberglass fabric manufactured by North American Textile Corporation. This fabric is an orthogonal plain weave with a count of 20 warp yarns by 15 fill yarns per 2.54 cm. The injection fluid was a general purpose Mobil DTE 24 oil. "Edge flow" regions were formed in the mold by shortening the width of plies 4, 8, and 12 in the preform stack from 7.62 cm to either 5.08 cm, 6.35 cm or 6.985 cm. Thus, in the edge flow regions along the length of the mold (widths of 2.54 cm, 1.27 cm, or 0.635 cm), there were only 12 fabric layers through the thickness. The fiber volume fractions were 51% in the 15 layer region, and 41% in the edge flow region. Permeabilities of the 41% and 51% regions were measured separately.

The measured permeabilities and volume fractions were used as input to the RTMFill code, and the predicted and measured flow front movement were compared. One such comparison is shown in Figure 3 (edge region 0.635 cm wide). A number of general observations can be made. The figure shows good qualitative agreement between experiment and the model predictions. The fluid progresses through the edge flow region at a much faster rate than through the main body of the preform, and the last point to fill is the far left corner of the main body region. However, a few quantitative discrepancies were noted. While the overall time to fill the entire mold matched very closely, in most of the experiments (but not all) the fluid progressed through the edge flow region at a faster rate experimentally than predicted numerically. This is evident in the figure which shows that fluid reaches the outlet wall in the edge flow region in 245 s experimentally, compared with a calculated value of 266.7 s.



Experimental Flow Front Position as a Function of Time



RTMFill Simulation of Flow Front Position as a Function of Time

Figure 3: Plots of flow front position as a function of time for injection into a mold with an edge effect region 0.635 cm wide. Experimental results are shown in (a) while simulations from RTMFill are shown in (b).

A further comparison of the experimental and numerical flow front progression was made by comparing flow front position vs. time, along both the right and left walls of the mold, for both the experimental and numerical cases. Agreement between the two is very good along the left wall of the mold. Along the right wall, agreement is very good up to a position of about 18 cm (7 inches), and then the two begin to slowly diverge. Although the deviations are not catastrophic, it does show that greater understanding of the nature of the physics of the flow in the transition zone is needed. Another difference between the experimental and numerical data is the flow front shape. Early in the experiment, the flow front shape in the main region of the flow has a characteristic "parabolic" curve to it. Later in the experiment a transition occurs and the shape becomes much more linear. This transition from parabolic to linear shape is not predicted numerically. The reasons for the discrepancies that arise are not clear at this point, but a number of possibilities, such as surface tension effects and fluid structure interactions (i.e., mold wall flexure), are being investigated.

PERFORMANCE - DURABILITY

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In the area of performance, the Composites Group focuses on durability. The approach follows five steps. First, samples are prepared with systematic variations in formulation and processing. Second, the samples are exposed to environmental factors such as moisture, temperature, and loads. Third, techniques such as spectroscopy are used to follow the chemical changes that occur. Fourth, the mechanical properties are studied with micro-tests that try to isolate the behavior of the resin, fiber, and fiber-matrix interface in simple, well-defined geometries. A good example is the single-fiber test methods used to study the fiber-matrix interface. Finally, macro-tests are performed on composites to see how the constituent behavior studied in the micro-tests translates into the composite. Active industry interactions are pursued in an effort to obtain assistance, particularly with the full scale composite tests, and to transfer the results to the market place.

During the past year, the efforts resulted in a new analytical technique to simplify data evaluation in the single-fiber fragmentation test. Several new programs were initiated that utilize this analytical method. In addition, a program that was begun last year to study moisture attack on composites became fully active. This effort is expected to grow because the topic is critical for many applications.. Finally, an effort to investigate compression strength in composites was conducted. The sections that follow will describe these three activities in more detail.

Micro-Tests for the Measurement of Interface Strength

As indicated above, an important aspect of the micro-testing program is the fiber-matrix interface, and NIST has implemented two of the single-fiber tests for interface strength: the fragmentation measurement and the micro-drop pull-off test. Part of the effort in the NIST program is to study these test methods using finite element analysis and other techniques. The goal is to determine exactly what the tests measure, what assumptions must be made, and what limits must be placed on the materials. In addition, ways to simplify the testing procedure are sought.

New Analysis Method: During the past year a new analysis method was developed to facilitate the evaluation of data for the fragmentation test. In calculating an interface strength from the test results, it is necessary to have a fiber strength, and this is very difficult and time consuming to measure. The fiber strength depends on length, so the value of interest is that corresponding to the very short length associated with the fragments in the test. This length is too small to measure directly, so a variety of lengths must be measured, and the data extrapolated to get the desired value. Moreover, fibers have a distribution of strengths, so a large number of tests must be run at each length and analyzed to determine an appropriate average.

The new analysis method which is based on the work of Wagner and others permits the estimation of both fiber and interface strength from the fragmentation data. Another advantage of this new analysis is that it facilitates use of the fragmentation test for environmental studies. As will be seen below, experiments on glass fiber-epoxy composites have shown that moisture can attack both the interface and the fiber. Unfortunately, it is difficult if not impossible to expose an isolated fiber to the environment that is present in a fragmentation sample placed in water for long periods of time. Consequently, the fiber strength cannot be determined independently.

In the fiber fragmentation test, a single fiber is placed down the center of a dog bone sample. The sample (and fiber) are then loaded in tension causing the fiber to break. The strain is increased until the fiber can no longer be broken into smaller fragments. This is called the saturation point. The lengths of the fragments are measured and an appropriate statistical analysis is applied to determine an average length. This is combined with the fiber strength to estimate the interface strength. In the usual analysis, only the fragment lengths at saturation are measured. The idea behind the new analysis is that before the saturation point is reached, the experiment can be viewed as conducting miniature fiber-strength tests on each fragment; i.e. the stress is increased and the fragment breaks. By taking data on the fragments during the loading of the sample, information regarding the fiber strength is obtained. Moreover, the lengths involved are short and therefore close to the appropriate value.

The new analysis method assumes the fiber strength follows a Weibull distribution and so the output is the Weibull parameters. To test the new method, the fiber strength was determined with fragmentation samples and with tests using the fibers themselves. A comparison shows good agreement between the Weibull parameters obtained with the two different procedures for two of the three fiber types tested.

New Programs Initiated: One objective in the durability program is to encourage the initiation of new projects that take advantage of the interface test facilities developed in the NIST program. During the past year, two new programs have been planned, and in both cases the ultimate goal is to understand durability issues. The first project involves using the two single fiber tests to determine interfacial properties of composites used in the dental industry. Good interface strength is believed to be important for the performance of these materials, and exposure to the environment present in the mouth places a great burden on the interface. Preliminary experiments indicate that the tests work quite well for the materials involved.

The second program planned is a joint venture with researchers (T. Donnellan, and R. Sposili) at the Grumman Corporation and will examine the effect of different fiber sizings (coatings) on the interface properties. The literature suggests that the modulus of the resin in the interface region can be changed by altering the sizing, and this appears to change the apparent interface strength. The literature results are inconsistent, however, and so further study is warranted. The Grumman program will also extend the study to include durability after environmental exposure.

The Effect of Moisture on the Strength of the Glass Fibers and the Interfaces/Interphases in Model Glass/Epoxy Composites

The study of environmental attack on composites was motivated by strong indication from industry that this was a widespread area of concern. Detailed follow-up discussions with industry, particularly the automotive companies, indicated that a primary mode of environmental attack on glass-fiber reinforced composites is degradation of the fiber-matrix interface. As a result, this topic was selected as the initial focus of the NIST program. The material system chosen for first studies was glass fibers in a model epoxy (DGEBA/mPDA). This system is simple and provides an excellent tool for establishing a testing protocol. In addition, this material is a good choice for a cooperative effort with Exxon since they are conducting similar experiments and are interested in glass-epoxy composites for off-shore oil rigs. A second model system using glass and polyurethane is being developed for a program now being organized with the Automotive Composites Consortium (Ford, General Motors, and Chrysler). Mark Greenwood from Owens Corning Fiberglass will be providing expertise on the fibers and fiber sizings.

To examine environmental attack on the interface, the program utilizes the five steps outlined in the introduction to this section. The initial focus is on micro-tests in which the single fiber fragmentation experiment is used to study samples that have been immersed in hot water for various periods of time. As indicated above, this test measures the lengths of fiber fragments at the saturation point, and the average value is called the critical length. The ratio of critical length to fiber diameter, L_c/D, is a measure of interface strength but also depends on the fiber strength. The new analysis procedure described above will permit the simultaneous estimation of both, but this analysis was not available for the data obtained last year. What can be said, however, is that an increase in L_c/D indicates that degradation of the interfacial properties is dominant, while a decrease shows that the degradation of the fiber strength is dominant.

Hydrothermal Exposure: Figure 4 also shows the data for exposure of E-glass/epoxy samples immersed in 75 °C distilled water for a maximum of 5,520 hrs. The L_c/D values increased from an average of approximately 22 to 36-38. Although some scatter in the data exists, this trend of increasing L_c/D indicated that the rate of interfacial degradation is greater than the rate of degradation in the strength of the fiber. In addition, the fragmentation profile (the normalized number of fragments as a function of applied strain) showed that the fiber in the hydrothermally treated sample fragmented and achieved saturation at a lower level of strain than that in samples that were not exposed to hot water. The T_g of the resin increased somewhat (5-8 °C) after 1,632 hrs of exposure, but after 5,520 hrs in hot water,

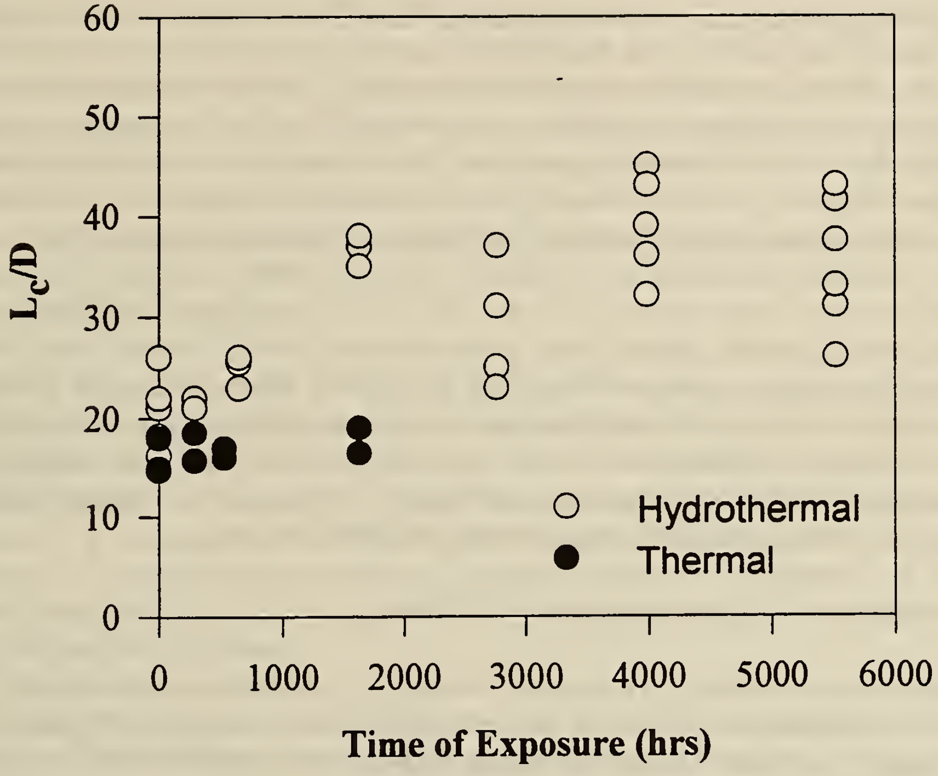

Figure 4: Plot of the L_c/D is shown as a function of time of exposure to thermal (75 °C, black circles) or hydrothermal (75 °C distilled water, open circles) conditions.

the T_g was similar to that for a sample that had no hydrothermal exposure. In general, it appears that these changes in the T_g did not significantly influence the results of the single-fiber tests. Changes in strength at the interface and in the fiber appear to be the major factors influencing the changes in the L_c/D values on hydrothermal exposure.

Thermal Exposure: For reference, Figure 4 also shows data for samples exposed to 75 °C for up to 1,632 hrs in a ambiant humidity (15-20%). These samples show no significant change in L_c/D even at the longest exposure time. Neither the appearance of the fragments nor the fragmentation profile showed any real change compared to E-glass fibers in samples that had no thermal exposure beyond the initial curing of the resin. It appears that the thermal treatment did not influence the interfacial properties or the strength of the fiber after 1,632 hrs of exposure. The thermal treatment resulted in approximately a 10-12 °C increase in the glass transition temperature of the resin after 1,632 hrs and an increase of 16-17 °C after 2,760 hrs. The variation in T_g could be due to a number of effects including chemical cross-linking and physical aging; however, this variation does not seem to have a major affect on the L_c/D for these samples. Future work will investigate this area further and expand the measurements to longer times.

Evidence for Environmental Degradation of the Glass Fiber: Fragmentation of the fibers in the hydrothermally treated samples reached the saturation point at lower values of applied strain than did the fibers in the dry or thermal environment. This result may suggest that the fiber was degraded by the exposure to water. Presumably, the alkali content in E-glass makes it susceptible to environmental degradation. Other results not presented here also suggest that fiber degradation may be occurring. To test this hypothesis, the distilled water used to expose the samples was analyzed for ions leached from the E-glass. The approximate composition of E-glass is, by weight: SiO_2 (52-56%), Al_2O_3 (12-16%), CaO (16-25%), MgO (0-6%), Na_2O and K_2O (0-2%), B_2O_3 (5-10%), Fe_2O_3 (0-0.8%), and TiO_2 (0-1.5%). Inductively coupled plasma mass spectrometry (ICP-MS) showed that the water contained measurably higher contents of Ca, Mg, and K than either the sample of water from the flask containing no samples or that from the flask containing epoxy samples without fibers. These results are consistent with water attacking the glass fiber and leaching out these ions, and hence, degrading its strength. (Gregory C. Turk of the Chemical Sciences and Technology Laboratory at NIST conducted the ICP-MS analysis.)

Compressive Failure of Polymer Composite Materials

The final activity in the Durability Task is an investigation of compression strength in composites. The compressive strength of polymer composites is considerably lower than their tensile strength, and is therefore the limiting factor in many applications. Also, while the tensile strength of such composites can be well-estimated from the properties of the constituent fibers and matrix, compressive failure is still not well understood from this micro-mechanics point of view. Besides the properties of the constituent materials (and the interface between them), the compressive strength is also influenced by the processing of the composite through fiber waviness or misalignment, as well as by the failure mode (such as micro-buckling or kinking), which may change with changing environment.

Investigations were conducted using a single-fiber specimen similar to that employed in the fragmentation test but loaded in compression. The results indicated that the fiber compressive strength is not a likely initiator of composite compressive failure for either carbonized PAN-based fibers or E-glass fibers. Whereas the compressive failure strain of composites is generally between 1 and 2%, the carbon fibers did not fail below 4% and the glass fibers remained intact to 10% strain under compression inside an epoxy coupon.

OTHER PROJECTS

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In addition to the activities described above, there were three projects that drew upon expertise in the Group but fell outside the major thrust areas. The first was the continuing effort for the Office of Consular Affairs at the U.S. Department of State to develop test methods for passport laminates. The remaining projects focused on the two-phase, toughened systems often used in adhesives and composites. In one case, micro-mechanics was applied to study analytically the relationship between morphology and strength. In the second case, experimental studies examined the role of morphology in fracture behavior.

Testing of Passport Laminates

The Office of Consular Affairs at the U.S. Department of State is responsible for the U.S. passports, and this responsibility includes choosing the plastic laminate that is used to protect the photograph and descriptive information on the inside of the front cover. The State Department requires the laminate to protect this data page from dirt, spills, and abrasions that can occur in normal use. In addition, the laminate must also resist illegal attempts to tamper with the photograph or data page. To help the State Department find materials that meet these requirements, NIST suggests, reviews, and conducts most of the tests used to evaluate prospective laminates.

Over the years, this program has developed nine tests to evaluate potential laminate systems. In October of 1993, NIST and the State Department held a Workshop for industry and government experts as part of the review process for these test methods. This meeting provided an opportunity for the attendees to get a detailed description of the tests and make suggestions for improvements. In general, the tests were viewed by industry as very appropriate; however, several important changes were suggested. Based on this input, a number of the test methods were modified to include the suggestions. Another important benefit from the Workshop was that companies gained information on what laminate features are most important, and this will help them produce better products in the future. Moreover, representatives from several other government agencies learned the latest developments for testing of security laminates.

In addition to the Workshop, NIST conducted tests on laminates for the 1993 solicitation. The goal of this effort was not only to decide which products best serve the government's immediate needs but also to set up a list of products that meet the technical requirements in the solicitation. With this list, the State Department can negotiate for the lowest cost. A final area of activity in the NIST program was the evaluation of a new material system which involves digital images on synthetic paper. This system is being considered for border crossing visas, but may also have significant potential for use in future U.S. passports.

Micro-mechanics Analysis of Strength Behavior in Two Phase Systems

Two-phase polymer systems are used in many applications. The included phase can be cylindrical as is the case in a fiber-reinforced composite, or spherical like many toughened polymer systems. The behavior of these systems depends on the details of the morphology, and micro-mechanics may help understand and predict the structure-property relationships. The model studied here consists of aligned cylinders which provides a direct comparison for material systems with cylindrical geometries and a first order approximation for spherical systems. The analysis considers the stress interaction between the cylindrical inclusion (elastomeric or rigid) and a surrounding micro-cracked matrix. The goal is to examine the role of inclusion size on the strength of the system.

The calculations are exemplified by two practical situations: highly compliant inclusion in relatively brittle matrix (rubber modified epoxy), and highly brittle inclusion (styrene-acrylonitrile copolymer) in compliant matrix (polycarbonate). Infinite rigidity (as, for instance, carbon fibers in epoxy) and zero rigidity (as, for instance, post cavitated rubber inclusion) are considered as well to illustrate the two extreme limits. A source of (possible) error in predicting the composite behavior is the residual stress due to thermal expansion mismatch between the two constituents and the cooling that occurs after the curing process. Such calculations can be included whenever the curing history is known.

The results suggest that for some combinations of inclusion and matrix moduli the composites strength is particle-size dependent. Specifically, it is found that when the inclusion is relatively rigid (with respect to the matrix) then an optimal inclusion size exists (scaled by the characteristic length of the intrinsic micro-cracks in the matrix) which maximizes the strength. When the inclusions are more compliant than the surrounding matrix, or when structural softening intervenes (like cavitation of the inclusion, or debonding from the matrix), it is found that the smaller the inclusion size the larger is the strength of the composite.

The Effect of Morphology on Toughness for Epoxies Modified with Dispersed Acrylic Elastomers

Rubber-modified epoxies are traditionally synthesized using soluble, reactive, liquid rubbers which phase separate during cure. Although this approach produces tough materials, it offers very limited ability to control morphology, and hence systematic experiments to study structure-property relationships are difficult. The work here attempts to address this problem by investigating samples made from dispersions of preformed rubber particles in an uncured epoxy resin. The use of insoluble rubber particles to produce toughened systems has been known for a long time, but the control of the particle size and stability has been difficult. Recently, however, more attention has been paid to latex and dispersion polymerization techniques of modification, and this approach permits the formation of controlled particle sizes in stable dispersions. To take advantage of this technology, a cooperative program was initiated with D. Hoffman from Dow Chemical Co. He provided dispersions of acrylic rubber particles formed in an uncured epoxy resin (diglycidyl ether of bisphenol A) by *in situ* free radical polymerization of vinyl monomers. Changing the chemistry and/or the dispersion stabilizer alters the average particle size. By diluting with various amounts of epoxy before cure, samples with different acrylic rubber concentrations can be produced. The diluted dispersions were mixed with 5 phr (parts by weight per 100 parts by weight of epoxy) piperidine and cured at 120°C for 16 hours. The resulting materials had virtually identical glass-to-rubber transition temperatures which suggests good phase separation. For samples with a constant morphology (average rubber-particle size of 0.5 μm), the toughness increased by 735 % as the rubber concentration was raised to 15 phr and then remained approximately constant up to 25 phr rubber. There was a transition in failure behavior with increasing acrylic concentration from brittle-unstable to ductile-stable crack propagation. Samples with average particle sizes of 0.5 μm and 1.5 μm had essentially the same toughness at 5 phr rubber. This suggests there is little effect of particle size in this range.

STRUCTURE AND MECHANICS

Goals

Lifetime, durability, and dimensional stability of polymers and polymer based composites are determining factors in the performance of these materials in diverse applications from automotive and infrastructure to electronic packaging and imaging applications. The goals of the Structure and Mechanics Group are to perform research into the mechanics of polymeric resins and its relationship to nano- and micro- structural features and to develop models of behavior that form the basis of the prediction of long term stability and performance. The group works to relate the results of its experimental and modeling research to the needs of the U.S. Polymer and Composites Industries to remain competitive in the Global Market.

Research Areas

The Structure and Mechanics Group performs research in three areas that impact on the understanding of the lifetime, durability and dimensional stability of polymers and their composites: 1) Physical Aging--glassy and semi-crystalline polymers, 2) Microstructural Characterization--small angle X-ray scattering (SAXS), wide angle X-ray scattering, solid state nuclear magnetic resonance (NMR), positron annihilation lifetime spectroscopy (PALS), 3) Composite materials--finite element analysis. The efforts in these three areas are coordinated with two long range goals: a) understanding the microstructure level events that cause failure and physical aging in combined thermal, moisture and mechanical environments, b) validating constitutive laws and implementing finite element analyses necessary to describe the mechanical and dimensional responses of polymers and composites subjected to thermo-mechanical histories typical of industrial processing histories and end-use environments. In addition, work is performed in a fourth area 4) Elastomeric Materials, Gels, and Molecular Rheology. This work includes studies of elastomeric materials that impacts specific applications of concern in the infrastructure and in finding environmentally benign material substitutes for fluids used in refrigeration and fire suppressant applications. Additionally, the group has addressed problems in structure and mechanical response of surfactant gels and the influence of chemical microstructure on the rheological behavior of polymer melts. Details of the Group's work are presented subsequently.

Industrial Interactions

The Structure and Mechanics Group interacts with U.S. industries in a variety of ways. They range from simple, informal interactions with individuals at specific companies, interactions with consortia, and collaborative works with industrial scientists to more formal arrangements such as memoranda of agreement for proprietary work, workshops and Cooperative Research and Development Agreements (CRADA's) with specific companies.

In the informal category, the group interacts with Tennessee Eastman to use NMR techniques to characterize cellulose triacetates, with IBM and MTI Industries to measure the coefficient of thermal expansion of thin films used in electronic packaging, with Eastman Kodak to study moisture effects on aging of polymers, with Xerox to study the effects of aging on the yield response of glassy polymers used in imaging applications.

More formally, the group has worked to improve the capabilities and usefulness of the 10-meter SAXS facility for industrial users. As this has taken place, the facility was used under memoranda of agreement with Mobil Chemical Company, Shell Oil Company, General Electric Corporation and W.R. Grace Company. Negotiations are underway to perform work with Armstrong World Industries. In addition, a user workshop was held in April of 1993. Also two CRADA's were successfully negotiated during the year. One, which began in October, 1992 was to perform research on the physical aging of nylon and was a joint CRADA among NIST/E.I. Dupont de Nemours/University of Delaware. This resulted in a post-doctoral fellow working in our laboratories for the year. The second was negotiated with Dow Chemical Company to study fracture incubation processes in engineering thermoplastics using SAXS and PALS. This work resulted in significant Dow funding towards the project and the placement of a post-doctoral level foreign guest scientist to work in our laboratories.

The purpose of industrial interactions are several-fold. In the simplest cases problems of mutual interest are pursued or information is exchanged on programs that both the industry and NIST find to be important. In the memoranda of agreement with the SAXS user facility NIST serves as a resource for the industries to perform proprietary experiments on sophisticated equipment not otherwise available to them. The CRADA's make possible the leveraging of industrial and NIST resources to promote work that is directed towards problems of industrial concern and can profit from the NIST expertise in specific areas.

Other Agency Interactions

Other government agency support includes funding by the Cold Regions Research and Engineering Laboratory of the Army Corps of Engineers to perform measurements of the large deformation elastic properties of elastomers used as paving joint seals. In addition, a multi-year U.S. Air Force contract to study the compatibility of elastomeric seals with Halon fire suppressant replacements, has developed into a study of swelling thermodynamics in supercritical conditions and evaluation of long term stability of elastomers in supercritical solvents. Support from the Naval Air Development Center is being used in a collaborative work on deformation and small angle x-ray scattering of structured elastomers.

FY 93 Significant Accomplishments

- A Cooperative Research and Development Agreement with E.I. DuPont de Nemours and the University of Delaware was signed in October, 1992 to study physical aging of Nylon® 66.

- A Cooperative Research and Development Agreement with Dow Chemical Company to study fracture incubation in engineering thermoplastics using SAXS and Positron Annihilation Lifetime Spectroscopy was signed in September, 1993.

- A workshop for users of the NIST 10 meter SAXS facility was held in April, 1993.

- A high pressure isopiestic facility for testing the swelling of polymers and elastomers in fire suppressant fluids was designed and built. Classical Flory-Huggins solution thermodynamics was used at low temperatures. Alternative models are being examined for the description of swelling in the supercritical state.

- Results from the positron annihilation lifetime spectrometer have shown that temperature and mechanical deformations induce resolvable annihilation lifetime changes while those changes in lifetime upon aging are not resolvable with the current equipment.

- Swelling measurements on the natural rubber/benzene and poly(dimethyl siloxane)/benzene systems using our sub-ambient pressure isopiestic facility confirm prior results from this laboratory that the Flory-Huggins interaction parameter χ is crosslink dependent. The temperature dependence of $\Delta\chi$ has been explored and found to have a very strong temperature and crosslink dependence. There is no current theoretical understanding of this behavior.

- In a NATO sponsored collaboration with the Instituto de Ciencia y Tecnologia de Polimeros in Madrid, Spain exploration of the structure of backbone smectic liquid crystalline polymers resulted in a thorough structural characterization of two liquid crystalline polyesters.

- Rheological and Dielectric studies were completed on polybutadiene samples having differing microstructures.

- A new theory of rubber elasticity was developed in which deviations from classical theory are explained.

- The theoretical treatment of the adsorption of a ring polymer onto a surface was completed.

- Codes for large scale computing of phase separation kinetics in polymer blends have been successfully implemented.

PHYSICAL AGING AND POLYMER PERFORMANCE

G.B. McKenna, J.M. Crissman, D.H. Vanderhart, C.R. Schultheisz, R.J. Schadt, P.H. Mott, I. Spinu, R. Grosfeld, D.H. Pan, D.A. Lewis, J.M. O'Reilly, Y. Leterrier, A. Perez-Castorena, J. Beckmann, M.Y. Chiang, H. Chai, C. G'Sell

Decoupling of the Mechanical and Volumetric Responses in Polymer Glasses

The work from this laboratory using the NIST torsional dilatometer[1] has continued in the past year by extending the range of experiments and considering the implications of prior work. In particular, two important findings have been emphasized in the past year and form the basis for future exploration into the non-isothermal, nonlinear viscoelastic behavior of polymers and their composites. First, the apparent rejuvenation of glassy structure by the application of large stresses or deformations does not appear to be related to changes in the volume of the sample when the large deformations are applied. This is contrary to the expectations of Struik[2] and others[3,4]. Second, the time scales characteristic of the volume recovery and the evolution of the mechanical properties [$\log(a_{te})$] do not seem to track with the volume of the sample. Rather it is observed that in up-jump experiments the volume attains its equilibrium value prior to the mechanical response and in down-jump experiments the opposite is found. These results have significant implications.

In the first instance, the observation that the underlying structure of the glass does not change when large mechanical deformations are applied is important and needs further discussion. The description of the physics of glasses has been the object of considerable effort for many years, yet a complete description is lacking. The finding that the underlying structure of the glass may be unaffected by large mechanical deformations or stresses should improve the understanding of glassy physics. The present interpretation of this decoupling of the underlying structure is shown schematically in Figure 1 in terms of a three dimensional surface with axes V, T, σ_{12}. This depicts on the V-T plane the normal glass transition behavior and the arrows show isothermal volume recovery with time. Mechanical deformation applied to the sample is depicted by translation along the σ_{12} axis as well. (The mechanical deformation is represented by shear because the hydrostatic pressure component of the stress does have an influence on the thermodynamic state of the glass. It is expected that the nature of the σ_{12} axis is more complicated and includes, at a minimum, the entire stress or deformation history.) Although there are changes in the mechanical response when the volume changes due to the "aging" of the glass, it appears that upon unloading the sample returns essentially to the volumetric state from which it was originally perturbed. The implication is that the underlying glassy structure is decoupled from the mechanical stimulus. This, if true, is important since it means that the description of the mechanical response depends upon the current glassy structure, but the structure does not depend on the current state of stress. While this is a somewhat simple picture, it has the advantage of simplifing the description of glassy materials because the volume (structural) recovery then depends upon the thermal history alone and not upon the superimposed mechanical history. Of course, the thermodynamic state depends upon more than the volume and our results

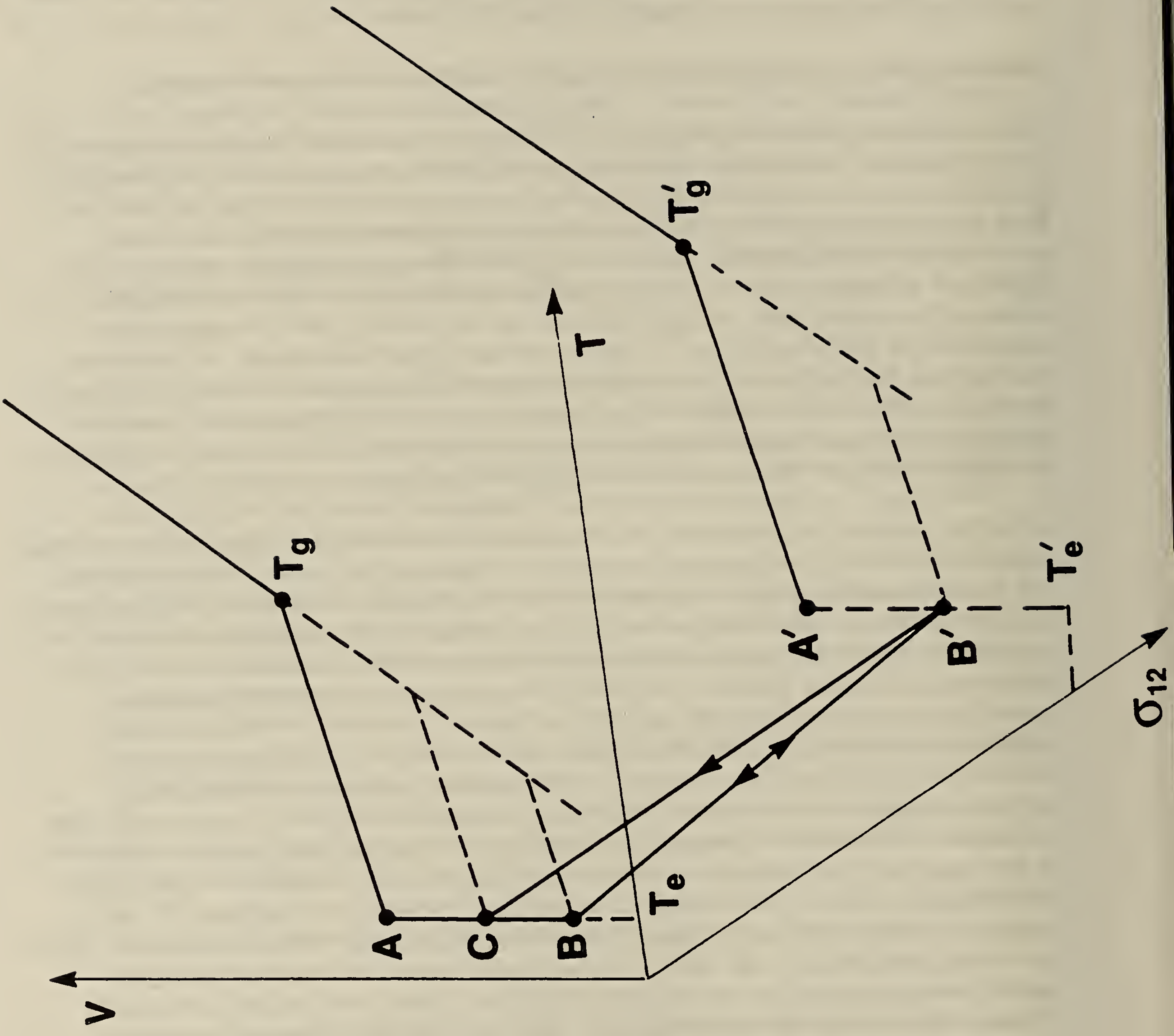

Figure 1

apply to only the volume. However, if the entropic (or enthalpic) contribution to the glassy structure is impacted by the mechanical stresses, then it is in some fashion decoupled from the volume recovery. Experiments in which the calorimetric response of a glass subjected to an isothermal aging history is measured simultaneously with the mechanical response are necessary to address this aspect of the problem. It is, of course, known[5,6] that the volume and enthalpy can recover at different rates.

The second finding is that the mechanical response after a temperature jump does not track the volume response. This is important because it suggests that a simple free volume interpretation of the evolution of the viscoelastic response is incorrect. To our knowledge, these are the first such results for the volumetric response, although there is a hint of it in the Kovacs, Stratton and Ferry[7] paper in up-jump experiments. In their experiments, however, the mechanical and volumetric experiments were not performed at identical temperatures. In other experiments, Roe, et al[8] found that in down jump experiments on polystyrene the enthalpy recovered to equilibrium prior to the mechanical response--the opposite trend to what is reported here for the volume. Hutchinson and co-workers[9] reported, for polystyrene, that the mechanical response in down-jump experiments tracks with the volume, while the enthalpy continues to evolve after the volume and mechanical responses have attained equilibrium. In all experiments, except those performed in the NIST torsional dilatometer[10-14], the measurements of volume(or enthalpy) were performed in parallel rather than simultaneously. But the evidence is mounting that the mechanical response does not track with the globally observable thermodynamic variables. This implies that the theoretical description of the nonequilibrium thermodynamics of glasses is imperative before one can completely understand or predict their structural and mechanical responses.

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Physical aging of semi-crystalline polymers--Nylon® 66.

The physical aging response of Nylon® 66 is being investigated under a CRADA with E.I. Dupont de Nemours and the Center for Composite Materials of the University of Delaware. This afforded an opportunity to extend prior investigations that focussed on aging of amorphous polymers to a semi-crystalline polymer. The materials chosen for study are a bulk, injection molded material and a thermally cast film material, with the current emphasis on the injection molded material. In past work on a nylon 6 material, Struik[1] observed aging in two regimes that were attributed to two different types of amorphous material--that with normal bulk amorphous properties and that constrained near the crystal surface. At this stage the present work can neither confirm nor refute this interpretation. However, the studies established that the glass transition temperature T_g as measured by differential scanning calorimetry (DSC) is not the temperature of demarcation between aging and non-aging behaviors. In particular, while the DSC T_g is approximately 50°C, aging behavior is observed from 41 to 65 °C. The typical time-aging time superposition, in which the essential feature of the evolution of the viscoelastic response is a shift in the characteristic time scale of the creep or relaxation, is observed at low strains and all temperatures to 65 °C. However, the time-temperature superposition generally observed in amorphous polymers in similar conditions[2] is not observed and at the highest temperatures time-stress superposition[2,3] is found to break down as well.

These studies are being expanded in the second year of the CRADA to effects at higher temperatures, further above the DSC T_g, and both above and below the T_g's obtained from dynamic mechanical measurements. In addition, the behavior of thin films, which can be expected to exhibit a significantly different morphology from the injection molded nylon, will be investigated.

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Effects of Moisture on the Behavior of Polymeric Glasses

Moisture is known to influence dramatically the mechanical response of polymeric materials. The influence of moisture on the behavior of glassy polymers is investigated through a variety of techniques. First, however, we are developing the hardware necessary to perform aging experiments under controlled relative humidity conditions. It is anticipated that the effects of aging due to relative humidity changes in the environment can be described in a fashion similar to temperature effects. Thus, preliminary work involves RH-jump experiments and monitors the aging response by sequentially applying small loads and performing time-aging time superposition on the creep-time curves obtained at increasing aging times. The slower diffusion of moisture into the sample after an RH-jump compared to thermal diffusion will make the data analysis more difficult than simple T-jump experiments. To the extent that moisture acts solely to plasticize the polymer, appropriate models are available to reduce the data. These experiments will serve to test the models.

In addition to the study of moisture effects on the mechanical response of the polymeric glasses, NMR is applied to the measurement of the mobility of water in polymer glasses. This work is also ultimately aimed at contributing to the Composite Durability project in the Composites Group by providing information concerning diffusion in the matrix and at the interface in composites.

Pulsed Field Gradient NMR Spectroscopy of Diffusion in Polymeric Glasses and Composites

Pulsed field gradient NMR (PFGNMR) employs a magnetic field gradient to impart a spatial tag to molecules by imposing a spatially-dependent Larmor frequency on the nuclei, often protons, within a sample. In addition, certain rf pulse sequences in NMR, including the so-called 'spin-echo' sequence, have a 'time-reversal' quality such that frequency-dependent phase development in one period is reversed during a second period. Therefore, at a particular point in time (the echo time) phase coherence is restored (even in the presence of such a distribution of Larmor frequencies) provided the Larmor frequencies for each spin remain fixed. Thus, when a spin attached to a diffusing molecule changes spatial coordinates, in conjunction with the application of field gradients, there is a loss of phase coherence at the spin-echo time. The amount of phase loss and the dependence of this loss on the echo time become sensitive indicators of the diffusional processes occurring in polymers and composite materials. PFGNMR has the capability, in systems like polymer melts, to probe displacements near a lower limit of 50 nm and diffusion coefficients to a lower limit of 10^{-11} cm^2/s.

This year hardware was acquired to perform PFGNMR measurements, a computer program was installed to evaluate various diffusional models in terms of measured spin-echo attenuation and a literature survey was conducted to identify polymer research problems which may be addressed by PFGNMR spectroscopy. Efforts have initially been devoted to the behavior of moisture in the glassy state of a cured epoxy identical to the one which is utilized by the Polymer Composites Group in investigations of glass fiber reinforced composites.

NMR Measurements of the Physical State of Water in a Cured Epoxy in the Glassy State

Prior to securing the PFGNMR apparatus, background experiments were preformed on the epoxy/water system to establish experimental parameters appropriate to the PFG measurements. The transverse relaxation time, T_2^H, for water in epoxy determines the upper limit on the time available for the PFG experiment. From knowledge of the maximum available strength of field gradients it was concluded that a minimum of about 5 ms were available to perform the PFG experiment. Experiments led to the conclusion that a temperature about 70 °C, or higher, was necessary. Below that temperature T_2^H is too short.

A second criterion for performing a successful PFG experiment is separation of the water-proton signals from the overwhelmingly larger signals originating from the polymer protons. (Water uptake in a typical epoxy is 3 - 4 % by weight.) Pulse trains were identified that enabled separation to a reasonable extent; however, this isolation procedure will always allow some fraction of the signal which belongs to polymer protons, rather than water protons. Incomplete separation should not cause major problems since the polymer protons do not diffuse to the same extent as water protons and the polymer-proton phase loss will not depend on the gradient strength in the PFG experiment.

Of keen interest is the physical state of water in an epoxy, and more particularly, whether water would have a single diffusion constant at any given temperature in the bulk solid. There is an extensive literature on the uptake of water in epoxy systems. Many authors have interpreted their data in terms of multiple sites for water, including hydroxyl groups and in some cases amino groups. Also, nonuniform crosslink density in a cured epoxy could lead to different levels of water penetration. Finally, several authors invoked the concept of voids or 'microvoids' to explain their data although estimates of the characteristic size of such features are generally not given. In the present work NMR techniques were used to probe the homogeneous character of water in epoxy. The observations reported below point to a uniformity of sites for water.

A. Proton line shapes-
   1. The line width of the water resonance decreases as temperature increases; moreover, there is no evidence for water having a shape arising from different populations of water with different line widths.
   2. The relative intensity of the narrower resonance is at least as large, and sometimes 10-20% larger than would be expected based on the known amount of absorbed water.
   3. The chemical shift of the narrow resonance in an epoxy with 3 wt. percent water is 3.1 ppm at 70 °C. This is 1.2 ppm below the value for bulk water at this temperature.

B. T_2^H for the narrow line: The T_2^H decay is exponential at 70 °C, and the line width implied by this decay accounts for over 90% of the observed line width, i.e. there is very little chemical shift dispersion.

C. Proton spin diffusion between narrow-line (water) protons and broader-line (epoxy) protons. Preliminary experiments indicate that at 70 °C water exchanges polarization (slowly) with epoxy protons and that the line shape of these epoxy protons, which have received their polarization from the water protons, is representative of the average epoxy signal.

The **conclusions** to be drawn from the above experiments are as follows:

1. On the time scale of about 200 μs and at room temperature, there are no water molecules which spend their time trapped in some void containing liquid like water.
2. At 70 °C, and on a timescale of 1-2 ms, all of the water protons, probably augmented by some hydroxyl protons, sample the same average dipolar fields, i.e. are found in similar average environments. Given that the diffusion constant at this temperature is about 10^{-8} cm^2/s, a typical water molecule would move about 100 nm in 2 ms; therefore, the variety of sites available to the water must be uniform on this scale of distance.
3. Since every different kind of site available to the water protons has its own characteristic chemical shift, the average shift is the time-weighted average over all of the sites visited. Averaged over the 2 ms timescale at 70 °C, the average shifts for all water protons are very similar, implying again that the average sites are uniform for all water molecules.
4. The 1.2 ppm difference in chemical shift between the water protons in the epoxy and in bulk water lies in the direction expected when water is taken from its own, strongly-hydrogen-bonding environment and dispersed in an organic matrix. At ambient temperature, the proton resonance from trace amounts of water in organic solvents appear at shift values in the 1.5 to 3 ppm range, compared to bulk water at 4.7 ppm. Thus, this shift difference suggests that water spends a non-trivial fraction of its time as a **dispersed** molecule, as opposed to a water molecule in a void filled with several other water molecules.

Although all of the above conclusions point to a uniformity of sites for water it is recognized that the time scales and distance scales associated with the observables still admit the possibility of substantial heterogeneities of sites on size scales below about 50 nm.

NETWORKS AND GELS

G.B. McKenna, J.M. Crissman, E.A. DiMarzio, J.F. Douglas, J.D. Barnes, W.K. Waldron, S.B. Baxter, J.M. Niemiec, F. Horkay, P. Terech, S.A. Ketcham

Elastomer Seal Compatibility with Halon Fire Suppressant Replacements

Halon 1301, tetrabromomethane, is used as a fire suppressant in civilian and military aircraft, as well as in other applications such as computer rooms. Owing to concern about its destructive impact on the ozone layer of the atmosphere, its use will be banned in coming years. In response to the problem, the U.S. Air Force sponsors efforts at NIST to evaluate replacements that are less harmful to the atmosphere and still are effective fire extinguishing agents. As part of the NIST effort, the Structure and Mechanics Group evaluates elastomer seal and lubricant compatibility with eleven fluid (See Table 1) materials that the Air Force has selected as potential Halon replacements.

Two approaches were taken to provide data relevant to the goal of selecting three fluids from the original 11 and 2 elastomers from the original 6. First, isopiestic (constant vapor pressure) measurements of the swelling of the crosslinked and uncrosslinked elastomers and the greases were performed to obtain thermodynamic data about the compatibility of each fluid with the elastomers and greases. Second, the elastomer durability and grease stability were examined after exposure to each fluid to 150 °C and for times up to 6 weeks.

Isopiestic Measurements

Six pressure vessels were designed and built for measuring the swelling thermodynamics under isopiestic conditions of three greases and six sets of crosslinked and uncrosslinked elastomers in the eleven fluid agents. The degree of swelling was determined by measuring the mass uptake of the agent or solvent using the quartz spring and cathetometer arrangement. The pressure vessels were designed for a maximum working pressure of 5.86 MPa (850 psi) with two view ports 180° apart for viewing and backlighting purposes. The view ports are made with 10.16 cm (4") diameter and 2.54 cm (1") thick circular plates of tempered borosilicate glass. The cylindrical vessel has 2.25 liters of inner volume (7" height by 5" diameter) and is large enough to admit a 7.62 mm (3") square by 15.24 mm (6") high spring stand with sixteen fused quartz spring and pan assemblies. Quartz springs with a coil diameter of 6.4 mm and either 1 mg/mm or 1.25 mg/mm sensitivity (spring rate) were used. The pans were 10-25 mg and were slightly curved with diameters of 7-9 mm.

Each vessel was placed in a 40.64 cm (16") diameter by 30.48 cm (12") high cylindrical Pyrex jar and immersed in a clear silicone bath oil with a viscosity of 50 cP. Each bath was heated using a 1000 W immersion heater and stirred to maintain temperature uniformity using a 134.25 kJ (1/20 hp) mixer with a 5.08 cm (2") propeller.

A pressure charging and recovery system was designed and built to allow the admission of the agent into the previously evacuated vessel and the recovery of the agent after each measurement. The system was also capable of over pressurizing the vessels with nitrogen, but this capability was not employed.

The elastomers used in this study were crosslinked and uncrosslinked sets of fluorocarbon, silicone, fluorosilicone, neoprene, and nitrile/butadiene copolymers with 15 and 45% polyacrylonitrile. Three fluorocarbon greases were also evaluated. The 15% acrylonitrile/butadiene crosslinked copolymer was prepared by first dissolving approximately 2 g of polymer in 50 ml of benzene. Next, 1 part per hundred (phr) of dicumyl peroxide was added and dissolved. The benzene was then allowed to evaporate and the specimen was placed in a oven at 149 °C for a period of 2 hours in order to crosslink the peroxide containing specimen. The 45% acrylonitrile/butadiene copolymer was crosslinked in a similar manner using pyridine after it was found that benzene was not an effective solvent.

The total number of experiments (11 fluids, 6 uncrosslinked elastomers, 6 crosslinked elastomers and 3 greases, 4 temperatures, 5 pressures) make a detailed discussion of the results beyond the scope of this summary. However, this series of experiments was successful in providing information about the potential swelling compatibility of the materials with the fire suppressant candidate fluids. Several important features have emerged to date. The fluids all pass through their critical point in the temperature range chosen for study. Therefore, the studies include a significant amount of data on swelling in both sub- and super-critical conditions. In sub-critical swelling, compatibility evaluations were based upon conventional Flory-Huggins solution thermodynamics and in the super-critical case, Flory's Corresponding States theory was used. In any event, in the super-critical experiments swelling was very small and the compatibility evaluations were based upon the swelling that occurred in sub-critical conditions by considering the relative values of the solvent/polymer interaction parameters.

Table 1. Halon 1301 Replacement Candidates.

TRADE NAME	CHEMICAL NAME	FORMULA
HFC-236fa	HEXAFLUOROPROPANE	$CF_3CH_2CF_3$
HFC-32/125	AZEOTROPE	CH_2F_2/CHF_2CF_3
HFC-227ea	HEPTAFLUORPROPANE	C_3HF_7
HCFC-22	CHLORODIFLUOROMETHANE	CHF_2Cl
HFC-134a	TETRAFLUOROETHANE	CH_2FCF_3
FC-116	HEXAFLUOROETHANE	C_2F_6
HCFC-124	CHLOROTETRAFLUOROETHANE	$CHFClCF_3$
HFC-125	PENTAFLUOROETHANE	CHF_2CF_3
FC-218	OCTAFLUOROPROPANE	C_3F_8
FC-31-10	DECAFLUOROBUTANE	C_4F_{10}
FC-318	OCTAFLUOROCYCLOBUTANE	cyclo-C_4F_8
CF_3I	IDOTRIFLUOROMETHANE	CF_3I

Durability Evaluation

In this instance the elastomers tested were in the form of o-ring seals purchased from a seal vendor, but of the same elastomer types evaluated above. The o-rings and greases were exposed to the fluids at 5.86 MPa (850 psi) and 150 °C for times of 1, 2, 4, and 6 weeks at which time the compression set, tensile modulus at 100 % deformation and breaking stress and strain were measured for each of the elastomers. The viscosity in a cone and plate geometry was measured for the greases. It was generally found that the selection of 150 °C was unrealistically harsh, with the result that virtually all of the elastomers degraded significantly within the longest time of 6 weeks exposure. The shorter time exposures allowed some discrimination among the elastomers and fluids, however, and several candidate fluids were definitely harsh environments, possibly because of contaminants in the nominally inert fluids. Also, the acrylonitrile-butadiene copolymers degraded significantly in all of the fluids after just two weeks of exposure. The greases, for the most part, showed little sign of degradation.

Future Work

The project is scheduled to continue for another 18 months during which time elastomers will be exposed to three of the fluids for long term durability. Also, a new fluid, CF_3I and a new elastomer type, EPDM will be evaluated. These latter two will be tested using the isopiestic measurement technique for swelling compatibility. The durability will be evaluated using lower temperatures of 50, 75 and 100 °C to establish activation energies for the degradation of the properties described above. The stability of the greases will not be further evaluated.

The Strain Energy Density Function of a Sealant: Measurements and Use in a Finite Element Analysis of a Seal

In a collaborative contract with the Cold Regions Research and Engineering Laboratory, work has been progressing to implement results from measurements of the strain energy density function made in the Structure and Mechanics Group into finite element codes for the deformation of paving joint seals. The joint sealants being studied are two commercial silicone rubber "self-leveling" materials. Single step stress relaxation experiments in torsion have been performed. The torque, normal force and strain are measured for times up to 1000 s. Current experimental work has been limited to strains below 1.25 due to the torque and normal force limitations of the apparatus available. (Work is underway to upgrade one of the torsional rheometers in the laboratory to increase the range of deformations attainable). The material response has been characterized at temperatures from -30 to 50 °C.

From the isochronal values of torque and normal force as functions of strain, the procedures of Penn and Kearsley[1] and Kearsley and Zapas[2] were adapted to determine the Valanis-Landel[3] (V-L) strain energy density function for the sealants. By making the assumption, demonstrated to be valid for natural rubber systems,[4] that the V-L function is a reasonable representation of the response of the sealants, one can calculate the stress-strain response in any other geometry of deformation, i.e., tension or compression. This is important because finite elasticity finite element codes, as available commercially, use input values from the stress-deformation response in several different geometries of deformation to obtain a useable strain energy density function, usually in terms of the invariants of the deformation gradient tensor, I_1 and I_2 . By performing torsional experiments in which the normal forces and torques are measured, one greatly simplifies the experimental task required to determine the material response functions.

The finite element codes were used to calculate the force-displacement behavior of representative butt joint seals in tension and compression. The results have been compared with analytical, but approximate, solutions that are generally used by the design community. Preliminary results indicate that interfacial stresses between the seal and pavement can differ by as much as 30% between the approximate solutions and those obtained from the finite element analyses. Because the lifetime of pavement joints depends upon seal integrity, calculations using realistic material parameters are an important contribution to the selection criteria and design criteria used in sealant applications for runways, highways, buildings, and other infrastructure related areas.

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Anomalous Swelling in Rubber and the Crosslink Dependence of the Flory-Huggins Interaction Parameter

Over the past 50 years there has been a considerable interest in the deviations of rubbery behavior from the classical theory. Apart from the observation that the elasticity of the dry rubber deviates from that of the classical theories, there has been considerable work to attempt to validate the Frenkel[1]-Flory-Rehner[2] hypothesis that the elastic and mixing contributions to the free energy are separable and additive. The problem with the determination of the FFR hypothesis validity arises from the need to independently measure the mixing and elastic contributions to the free energy of the swollen network and compare them with measurements on the uncrosslinked rubber and/or the dry network within a correct framework.

In prior work in this laboratory[3-5], measurements of the mechanical and swelling properties of crosslinked natural rubber suggested that the Flory-Huggins[6] interaction parameter χ is dependent on the crosslink density of the network. Furthermore, data from work by Gnanou, et al[7] on poly(ethylene oxide) networks (in which mechanical and swelling measurements were analyzed) suggested[5] a similar crosslink dependence of χ. Also, an analysis of the swelling activity parameter S and the data of Gee, et al[8] for a similar natural rubber suggests a crosslink dependent χ based on the fact that S is non-zero at zero swelling[5]. More recently, experiments were undertaken in this laboratory[9,10] to measure S for polyisoprene networks having different crosslink densities in order to examine the question of the crosslink dependence of χ and also the anomalous peak in the value of S as the degree of swelling increases. These results suggested that the anomalous peak in S is only anomalous in that it appears and disappears over narrow temperature ranges and can depend on solvent. This behavior is inconsistent with any current theory.

During the past year further isopiestic measurements of solvent uptake by crosslinked and uncrosslinked rubber were made, S calculated from these measurements and the data at low degree of swelling used to show that χ is a crosslink dependent parameter. While these results are consistent with those found previously, they differ in that the swelling is at low values of solvent activity. This suggests that, while the volume fraction of rubber may play a role in the apparent crosslink dependence of χ, it is definitely not the only parameter. Finally, it was found that the sensitivity of χ to crosslink density is strongly temperature dependent. At low temperatures for the isoprene-benzene system, there is a strong crosslink dependence of χ, while at higher temperatures the dependence on crosslink density decreases dramatically.

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A New View of Rubber Elasticity

Work in the Structure and Mechanics Group has continued to explore alternatives to the classical theories of rubber elasticity, which are generally acknowledged to be inadequate in describing the behavior of macromolecular networks, particularly in the bulk state. Recent work in the group resulted in the development of a new model in which the strain energy density, W, of the dry, unswollen rubber contains non-classical contributions in that W depends on $(\lambda_x+\lambda_y+\lambda_z)$ and $(\lambda_x\lambda_y+\lambda_y\lambda_z+\lambda_x\lambda_z)$ which previously had not been used on the basis of symmetry arguments that are no longer considered valid. Generalization to swollen rubbers and gels are to be considered in the future.

"Living Polymer" Networks in Organic Solvents

Studies in the Structure and Mechanics Group have also looked at small molecule systems that exhibit polymer-like and gel-like behavior. Viscoelastic solutions of a bicopper tetracarboxylate complex in tert-butylcyclohexane have been studied by dynamic mechanical measurements in a wide range of concentrations (0.4-15.5 % volume fraction). The zero shear viscosity, the elastic modulus, the terminal relaxation time and the height of the high-frequency dip in a Cole-Cole representation of the complex elastic modulus follow scaling laws. The related exponents have been analyzed in the context of the physics of "living polymers": a term used to describe worm-like species undergoing scission/recombination reactions that compete mainly with the long time motions of the polymer-like chains. The system studied was made up of molecular threads approximately 1.75 nm in diameter of $Cu_2(O_2C\text{-}CH(C_2H_5)(C_4H_9))_4$ in the apolar solvent. Such a system is typical of a "living polymer" where, instead of mechanisms involving transient polymeric crosslinks, a reversible chain scission mechanism prevails. The dynamics in the high-frequency range evolves from a regime where the terminal chain relaxation is the dominant mechanism of relaxation to a cross-over regime where "breathing" fluctuations and Rouse motions become important. Large modifications of the stress relaxation function occur for more concentrated systems due to a topological conflict between the mesh size of the network and the persistence length of the chains. In this situation, the stress relaxation tends to that of more unbreakable and polydisperse chains. The current binary system is the first example of a living polymer in an organic solvent and exhibits elastic moduli ($G \approx 120$ N/m^2 at a concentration of 1%) which are at least 20 times larger than those found for the aqueous living polymer systems.

MICROSTRUCTURAL CHARACTERIZATION-Small and Wide Angle X-ray Scattering and Nuclear Magnetic Resonance

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Small Angle X-ray Scattering and Pole Figure Facilities

Introduction: The NIST Small Angle and X-ray Pole Figure Facilities are increasingly used by industrial, national laboratory, other federal agency and university clients. At the same time, the facilities are contributing directly to research projects within the Structure and Mechanics Group. Significant efforts are also being expended to upgrade the facilities.

Facility Upgrades: The 10-meter Digital SAXS Camera had an important software upgrade that significantly improved its productivity and ease of use. The image histogramming and control of data acquisition are now carried out on a desk top computer whose graphical user interface makes it easier for inexperienced users to operate the camera. The raw data file formats have been redesigned to enhance portability and compatibility with commercial visualization software, thus allowing users greatly improved ease of interaction with their data in their home laboratories.

The FORTRAN codes for reducing the SAXS data have been ported to a workstation that provides much greater speed in numerical computations and enhanced capability with respect to data visualization. The new codes are significantly more portable than those they replaced. This will allow interested users to carry out more data reduction off-site.

Modern networking methods are being implemented to connect the workstations with the data acquisition system. This provides immediate access to the data, even from remote sites.

The software upgrades described above were accomplished with little or no down-time through combined in house work with a software subcontractor.

Outside Use of Facility: The industrial user base shrank somewhat during the past year. However, the total number of hours of service that the facility saw with outside users, industrial and other government laboratory, remained the same as last year because some of the individual projects were larger in scope. Efforts continue to maintain and grow the user base to support U.S. industry.

Internal Projects: The internal usage of the facility has been significantly higher than in the past as the SAXS facility has served to support projects within the Structure and Mechanics Group as well as elsewhere in the Polymers Division. This interaction has been partly accomplished from enhanced efforts to reach out to other researchers and by efforts to exploit the capabilities for research related to structure/property relationships within the group.

An important theme in the interactions within the Division and with the Reactor Radiation Division has been the exploitation of the complementarity between SAXS and SANS at larger scattering angles (Porod Law region) where SANS practitioners need additional data to resolve the interference created by incoherent scattering. This has led to increased emphasis on studying the limiting power law behavior ($I \propto q^{-n}$).

Experience gained in these efforts led to an evaluation of ways in which the camera configurations available in the 10-meter digital SAXS camera can be optimized to improve the signal-to-noise ratio of data obtained at q values of interest in studies of limiting power-law behavior. It was concluded that a second camera using a shorter collimation length would give increased signal strength that would be very useful in such studies. The ability to measure both low q and high q SAXS patterns with minimal changeover time should prove to be very attractive to users of the SAXS facility.

During the past year several topics were addressed using the SAXS facility. Within the Structure and Mechanics Group topics included molecular mixing in blends of cellulose and synthetic polymers in conjunction with solid state NMR measurements and gel formation and structure in small molecule gel formers. The latter subject is discussed below. In collaboration with members of the Polymer Blends and Processing Group the structure of dendrimers and the microstructure of block copolymers was investigated and with the Reactor Radiation Division, studies examined the microstructure of graphitized materials and the creation of pores in mechanically deformed solid propellants. Finally, the SAXS facility forms the core facility to be used in a CRADA developed with DOW Chemical Company to study fracture incubation in engineering thermoplastics.

Organogels and Aerogels of Racemic and Chiral 12-Hydroxy Octadecanoic Acid

In collaboration with workers from the ILL in Grenoble, a study was made of the structure of racemic and chiral gels of 12-hydroxy octadecanoic fatty acid (12-HOA) in organic solvents. The long and short-range length correlations were investigated with both small and wide angle (x-ray and neutron) scattering, respectively. The cross-sectional shapes and sizes of the fibers found in the racemic systems are very similar to those observed in chiral gels and can vary from a square of ≈ 20 nm on a side, involving approximately 41 molecules per 0.1 nm of fiber, to a rectangle and even flat ribbons of 30 nm thickness. The 3-D gel network is strengthened by monoclinic crystalline nodes where the long and rigid fibers merge. "Head to head" contacts between the carboxylic head groups and growth of multiple H-bond sequences are constant features of these gels. The variations in the molecular ordering of the chiral and racemic systems in various solvents were analyzed and the scattering behavior of "crystalline gels" detailed.

Secondary Standards

Efforts to create secondary standards for intensity calibration received a boost with the recognition that certain fluorinated ethylene-propylene copolymers exhibited scattering patterns that could provide a good basis for measurement of the scattering invariant. SANS work carried out in the Reactor Radiation Division also demonstrated that this material scatters coherently in the q range of interest. The commercial materials used in these studies exhibit significant anisotropy, which may interfere with measurements of the scattering invariant on some instruments. The search for other fluorinated materials and alternative methods of sample preparation in order to overcome this difficulty are underway.

Workshop: A workshop on Small Angle X-ray Scattering held in April of 1993 attracted a number of current and potential users. The new data acquisition software and export file formats were demonstrated. The response to the limited amount of hands-on training that was provided as part of the workshop indicates that more activities of this kind may be desirable. Since the new data acquisition software operates on a type of desk top computer that is commonly available, an educational version of the program will be developed to allow users to practice camera operation and data analysis before actually coming to NIST to perform experiments.

NMR Characterization of Backbone Smectic Liquid Crystalline Bibenzoates

A NATO sponsored collaborative effort with Ernesto Pérez of the Instituto de Ciencia y Tecnologia de Polimeros in Madrid, Spain investigates smectic liquid crystalline (LC) polymers having mesogens incorporated into the polymer backbone. These LC polymers are polyesters which are condensation products of bibenzoic acid and aliphatic diols, the latter forming the spacers. Two closely related LC polymers have been of most interest, P7MB, in which the spacer consists of 7 methylene groups, and PDTMB which contains a more flexible spacer made by replacing the central methylene group of the heptane linkage with oxygen. Both of these materials form the smectic LC phase and both will also crystallize, albeit PDTMB crystallizes with much more difficulty.

A combination of X-ray, synchrotron, DSC and NMR data led to the following conclusions: a) The LC state is characterized by substantial dynamic disorder at room temperature. The spacer shows motions at frequencies in the MHz range and the mesogen, being more sluggish, displays motions in the low kHz range. Furthermore, the motions of the aromatic rings are more complex than simple 180° flips, thereby implying that a proper description of the mesogenic layer must include some dynamic disordering. b) Crystallinities which could be developed by lengthy annealing from LC precursors fell into the range of 0.3 to 0.4 in spite of levels of LC content in the precursors near 1.0. c) The development of crystallinity, starting with a LC precursor, caused a small change in the position of the lower-angle peak associated with layer spacing in the synchrotron and X-ray data. It was presumed that the change was a manifestation of the c-axis repeat distance of the crystal and a simultaneous broadening or disappearance of the LC layer line. This, along with the disappearance of a peak in the DSC associated with the isotropization of the LC phase, led to the speculation that the crystal growth caused disordering in those regions, formerly LC, outside of the crystallites. More support for this point of view came from changes in NMR relaxation times for carbons in the LC phase versus carbons in the non-crystalline phase of the annealed samples. d) The observations noted in points b) and c) imply that the LC phase is **not** a phase which demands a low topological defect content in order to form. Since the monomers can be far from their extended conformation and still satisfy the layer spacing, it is possible, in principle, to maintain the layer spacing in the presence of chain entanglements and even loops. Hence, in contrast to the nematic LC precursor case, the development of crystallinity from smectic LC precursors is not likely to lead to high crystallinities. Moreover, the growth of crystallites tends to force chain defects into the regions which were smectic. The increased density of defects injected into these regions is thought to create a disordering of this non-crystalline material and a broadening of any X-ray layer-spacing line arising from mesogen/spacer segregation in these regions.

Finally, ^{13}C spectra of the crystalline phase of each of the annealed samples were obtained. From these spectra, some information about the geometric disposition of the mesogens and the conformation of the 7-methylene spacer was inferred.

Intimacy of Mixing in the Miscible Blend, PS/PXE

Last year the results of proton spin diffusion studies of certain polymer blends were reported. Normally, spin diffusion data are useful for characterizing the average domain size along the thinnest dimension in a phase separated polymer blend. Stoichiometric information pertaining to phase composition may also be obtained.

Blends of poly(styrene) (PS) and poly(xylylene ether) (PXE) are considered to be thermodynamically miscible over the entire composition range. Spin diffusion data on a 50/50 blend contain, in principle, information about the average number of PS residues surrounding a PXE residue and vice versa. In practice, it is difficult to extract exact numbers; nevertheless, based on the spin diffusion data, it was determined that nearest (unlike) neighbors certainly exist around a given residue. Moreover, considering that chain continuity demands that at least two nearest neighbor positions have like residues, the average number of unlike residues occupying the remaining nearest-neighbor positions, is at least the number expected on the basis of the respective numbers of residues.

NMR Investigation of Polymorphism in Cellulose Triacetate and Its Oligomers

This project is a collaborative effort with John Hyatt of Eastman Chemicals, and R.H. Atalla of the Forest Products Laboratory of the USDA in Madison, WI. Eastman Chemicals produces cellulose triacetate (CTA) as a film substrate. CTA is often produced in states of low crystallinity and part of the reason for its dimensional stability is that it is very sluggish in developing crystallinity. Nevertheless, CTA has two known crystal forms, CTA(I) and CTA(II). These two forms are also related to the two allomorphs of cellulose, namely cellulose (I) and cellulose (II) in that, by heterogeneous acetylation, one can go from cellulose (I) to CTA(I) and back again, by heterogeneous saponification, to cellulose (I). The same processes connect cellulose (II) and CTA(II). The crystal structures of CTA (I) and CTA(II) are still matters of debate, although some have been proposed. The problem is that structure-relevant data derived from x-ray fiber patterns provide only limited information regarding structure distinquishing features between CTA(I) and CTA(II). Also, there is a wide variation in the rates of heterogeneous acetylation, depending on the natural source (e.g. wood, cotton, bacterial, algal) of the cellulose.

The original goal in this study was to compare the ^{13}C NMR spectra of several oligomers of cellulose and identify those oligomers which would have a structure parallel to the polymeric CTA. Eventually, this information could be used to select a material for growing a single crystal suitable for an X-ray structure determination. By this means, information about the structure of one of the CTA allomorphs could be deduced. Impact of this approach goes well beyond solving for a crystal structure. The issue of chain polarity in cellulose I and II has not been settled and CTA(I) and CTA(II) are close relatives. There are proponents of the idea that cellulose (I) has parallel chains and cellulose (II) antiparallel chains. In industrial processes, e.g. the production of rayon, cellulose I is converted to cellulose II. If this conversion involves switching the polarity of chains, then a much deeper understanding regarding the variation in processing requirements for celluloses of different origin would be at hand.

Studies on CTA oligomers from the dimer through the nonamer showed that the structures of the pentamer through the nonamer were strongly related to the CTA(I) crystalline form. A second study involved characterization of CTA samples prepared from cotton and ramie (a grass) celluloses with different histories of mercerization and heat treatment. In addition to verifying certain points already noted in the literature, these studies led to the recognition that the CTA chains move very sluggishly and require annealing temperatures of 220 °C in order to form well defined crystals. This insight, together with several other plausibility arguments led to the view that CTA(I) has parallel chains and CTA(II) has antiparallel character. Owing to sluggish chain mobility, the crystal form developed by heat treatment in the solid state is determined by local chain statistics of polarity. This means that the polymer CTA(I) will only form when the probability is high that the parent solid CTA has a high probability of clusters of parallel chains. By implication, the suggestion is strong that cellulose (I) and (II) have chain polarities corresponding to CTA(I) and CTA(II).

OTHER PROJECTS IN THE STRUCTURE AND MECHANICS GROUP

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Rheological Measurements and Dielectric Spectroscopy of 1,2-1,4 Polybutadienes

A collaborative effort with workers from the Forschungszentrum, Jülich consisted of rheological and dielectric studies on polybutadiene melts having different chemical microstructures as measured by the 1,2-vinyl content, ranging from 7 to 95%. The most striking effect of this modification of the microstructure is the continuous change of the glass transition from -100 °C to 0 °C as the vinyl content increases from 7 to 95 %. Rheological and dielectric spectroscopy were used to examine more subtle effects.

The rheological experiments were performed in the Structure and Mechanics Group using a rotary rheometer in both dynamic mode [to measure $G'(\omega)$ and $G''(\omega)$] and in stress relaxation [to measure G(t)]. The steady shear viscosity was also measured for the systems as a function of temperature from approximately T_g-10 to T_g+100 °C. Time temperature superposition was applied to the data and the KWW stretched exponential function was used to analyze the relaxation function in the glassy dispersion.

The same samples were used for dielectric time-domain spectroscopy experiments in the Electronics Applications Group. Time-domain spectroscopy experiments in the range 10^{-5} to 300 s were Fourier transformed to get the complex dielectric functions over 6 1/2 decades of frequency.

Several conclusions were reached concerning the effects of microstructure on the chain dynamics. First, the breadth of the glassy dispersion, as determined by the exponent in the KWW function, increases as vinyl content increases. Transition maps of peak frequency versus 1/T show that the relative behaviors of the glass transition α peak and the sub-glass β peak vary depending on the vinyl content of the chain. Also, close examination of the time-temperature superposition of the data show that the polybutadienes studied here do not strictly follow thermorheological simplicity. These results are currently being analyzed in the context of the Ngai[1] coupling model which relates the shapes of the glassy and terminal relaxations to their temperature dependences. Preliminary analysis suggests that this model does not strictly describe the data.

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Computer Simulations of Chain Dynamics and Phase Separation Kinetics

The Structure and Mechanics Group supports other activities in the Division through off-lattice computer simulations. Two projects have been successful in the past year: one to examine the effects of excluded volume on the relaxation behavior of polymer chains, the other to look at the kinetics of phase separation in polymer blends.

The effects of constituent volume and chain connectivity upon the motions of random coil polymer chains were studied by computer simulation of the dynamical behavior of simple bead-stick models of from 9 to 99 beads. Long internal relaxation times were obtained for chains with bead diameters from zero to 0.93 times the stick lengths. Moves were forbidden which would have resulted either in bead overlap (excluded volume) or in one stick passing through another (chain connectivity). In the extreme case of zero bead diameter, where there is no expansion of the chains by excluded volume, the extra exponent for the power-law dependence of the long relaxation time upon chain length is approximately 0.07. As bead diameter is increased, the exponent also increases until the bead diameter is equal to the stick length, at which point the exponent reaches the value of 0.48 established by prior work.

The dynamical behavior of dense systems of off-lattice models of polymer chains is being studied by computer simulation. Bead-stick models of freely jointed chains are employed, with hard-sphere repulsions (excluded volume) and finite attractive square-well interaction potentials between beads. A simple random bead-jump algorithm is used to simulate chain motion. These models were used to study the onset of phase separation in two-component blends after quenching. Each system to be studied is first brought to pre-quench equilibrium by running the simulation for a time long with respect to the longest internal relaxation time. The system is then quenched by changing the interaction potentials. The phase separation kinetics is studied by sampling scattering functions and mean-square interbead distances as functions of time elapsed after the quench.

Lattice Simulations of Polymer Molecules of Differing Architecture

Understanding the behavior of polymer molecules of differing architecture can be important as new synthesis techniques lead to molecules having unique properties. In the Structure and Mechanics Group, lattice models have been developed to examine the behavior of ring-like molecules near to surfaces and to study the mixing of plate-like and rod-like molecules in a solvent.

The theoretical treatment of the adsorption of a ring polymer onto a surface has been developed using a lattice model. The polymer is confined to walk on a lattice of M layers. The treatment allows simultaneously for adsorption energies of the polymer for each of the layers as well as the internal stiffness energy. These attributes are necessary to a self-consistent theory of bulk ring systems as well as for a theory of adsorbed rings.

Work is also being completed to generalize the lattice model of polymers to treat systems of compact molecules such as plates, cubes and thick rods. The calculation allows for various concentrations, molecular weights and orientations of the molecules. The thermodynamic properties of mixtures of plates and solvent have been calculated. This system shows a phase transition from randomly disordered to aligned plates that is much like the isotropic to nematic phase transition in rigid rod polymers. For squares of edge length to thickness ratio r the transition to the aligned phase occurs at a volume fraction V_x given by $rV_x = 2.7$. For rigid rods of length x the transition is given by the relation $xV_x = 5$. This work is useful for calculating the equilibrium properties of discotic systems, polymer-layered silicate composites and the adsorption of plate-like molecules.

Simulations of Spinodal Decomposition of Chemically Reactive Binary Mixtures

In support of the efforts in the Blends and Processing Group, the Structure and Mechanics Group is carrying out large scale simulations of the spinodal decomposition of chemically reacting binary mixtures. A Cahn-Hilliard- type model for a phase separating binary mixture undergoing chemical reaction is used and the linearized theory and computer simulations show that the initial long-wavelength instability characteristic of spinodal decomposition is suppressed by the chemical reaction $A \rightleftarrows B$, which restricts domain growth to intermediate length scales even in the late stages of phase separation. The final domain size R_F scales with the reaction rate Γ as $R_F \sim (1/\Gamma)^s$ where s is related to the exponent characterizing the domain growth in the absence of chemical reaction. The behavior exhibited by this model is similar to behavior observed in microphases separation of block copolymers.

POLYMER CHARACTERIZATION

The goal of the Polymer Characterization Group is to develop measurement methods, data, and standard reference materials needed by U.S. industry, research laboratories, and other federal agencies to characterize polymers for processibility, properties, and performance. The molecular weight and molecular weight distribution are the predominant molecular characteristics of polymers that affect their processing, properties and performance. The Group works with industry and standard organizations to identify current needs for standard reference materials. Based on these needs research on characterization methods and measurements are conducted leading to the certification of standard reference materials. Standards are produced for calibration of gel permeation chromatographs, the principal method used by industry for assessing molecular weight and molecular weight distributions, and melt flow standards that are used in the calibration of instruments used to determine processing conditions for thermoplastics.

The Group assists other programs of the Polymers Division by applying expertise in measurement method development and polymer characterization. An example is exploration of optical and fluorescence methods to monitor important polymer properties during processing. The objective of the polymer processing program in the Polymer Blends Group is to utilize this measurement technology in conjunction with process models to predict and control the materials properties and performance of final products. In addition, the Group collaborated with the Dental and Medical Materials Group to develop a fluorescence method for cure monitoring of dental composites, and with Enimont America to develop a fluorescence method for in-line monitoring of a microwave cure process.

Externally funded work in metal-polymer interactions focuses on determination of the reaction mechanisms involving toxic species and biopolymer systems with which they interact. With support for EPA and NIH, and in collaboration with University of Maryland at Baltimore, work is conducted on the stability of well-characterized lead solutions in polycarbonate containers and watering bottles. Liver and kidney tissue samples from animal toxicity studies have been examined for total arsenic and/or indium.

FY 92 Significant Accomplishments

- Absolute molecular weight measurements on narrow molecular weight distribution polyethylene oxides were made and resulted in certification of two standard reference materials to be used as calibration standards for aqueous size exclusion chromatography (SEC).

- A polyethylene molecular weight standard commonly used in SEC calibration and as a melt flow standard, was recertified. Melt flow measurements are used by industry to assess the processibility of thermoplastics.

- A convenient technique to detect metal-containing proteins was designed and demonstrated using metallothionein, a protein containing both cadmium and zinc. The principal components of this analytical system are a size exclusion liquid chromatographic system coupled to a graphite furnace atomic absorption spectrophotometer and variable wavelength ultraviolet detectors.

- As part of a collaborative effort with the University of Maryland at Baltimore, concentrations of lead dosing solutions (50, 250 and 1000 ppm) were regularly determined during a two-year study on the effects of lead on kidney function in rats. All data were statistically analyzed for their variance and normally found to be within 5% of their target values. The relatively small number of outliers never deviated by more than 10 to 15% of the target value.

STANDARD REFERENCE MATERIALS

C. M. Guttman, J. R. Maurey, C. C. Han, and P. H. Verdier

Aqueous SEC Molecular Weight Standard

No standard reference materials (SRM's) are presently available for water-soluble high polymers which are industrially important in such areas as adhesives, coatings, paints, lubricants, oil resistant plastics, etc. The need for standards for these materials has been noted by the Assessment Panel for the Materials Science and Engineering Laboratory, staff of industrial characterization laboratories, and in the responses to market surveys.

By far the most pressing need for water-soluble molecular-weight polymer SRM's is for calibration standards for aqueous size exclusion chromatography (SEC). The polymer selected for these standard reference materials is polyethylene oxide which should be usable on most aqueous SEC columns without special column conditioning .

Absolute molecular weight measurements on narrow molecular weight distribution polyethylene oxides were made and resulted in certification of the following standard reference materials. SRM 1923 is a polyethylene oxide with a weight average molecular weight of 27,000 and SRM 1924 is a polyethylene oxide with a weight average molecular weight of 121,000. Certificates have been issued on these polymers and a report describing their certification and use in calibrations is currently being written in preparation for their release by the NIST Standard Reference Materials Program (SRMP).

SRM 1475 Recertified

SRM 1475, a polyethylene molecular weight standard commonly used in SEC calibration and as a melt flow standard, was recertified. The old and new materials were compared using Size Exclusion Chromatography and the melt flow of the old and new SRM 1475 were measured. A report on this recertification is in final review.

Polyolefin Melt Flow Rate Standards

Melt flow rate and melt index measurements are used in the specification of polymers in industry. NIST SRM's with certified melt flow rates are used to check equipment stipulated by the ASTM D-1238 voluntary standard.

A branched polyethylene, SRM-1473, with a melt flow rate of about 2.0 g/10 min was recertified and a report was issued this year. This work was supported by SRMP.

METAL-POLYMER INTERACTIONS

K. L. Jewett, W. R. Blair, and F. W. Wang

A key mechanistic feature in the reactions between toxic metals and biosystems may involve the reaction of metals at specific sites. Such reactions may alter the functionality of the biopolymer. Since the bioactivity of proteins is dependent not only on their chemical compositions but also their three-dimensional structural features, a better understanding is sought of how metals bind to these biopolymers. Analytical procedures are under development that will lead to a better understanding of biopolymer-metal binding processes in mammalian systems.

Intracellular Chemical Speciation of Lead: Relation to Nephrotoxicity

When ingested, lead acts as a neurotoxic agent. Small children are especially vulnerable to the effects of lead poisoning and are generally at significant risk from lead exposure in urban, suburban and rural geographical locales of this nation. Current work examines lead-biopolymer binding at the molecular level.

A collaborative study with University of Maryland at Baltimore (UMAB) seeks to determine how lead is distributed in various tissue samples primarily including mammalian kidney, liver and blood samples after laboratory rats were permitted to consume various concentrations of lead solutions. Results from aqueous size exclusion chromatography (SEC) coupled to atomic absorption (GFAA) and multiple wavelength uv-visible (UV) detectors have shown which molecular weight fractions are selectively binding the metals. Moreover, important information on metal-protein binding constants may be obtained by this approach.

Protection of Archival Records

C. M. Guttman, D. Johnsonbaugh and K. L. Jewett

Protection of records stored in the National Archives and Records Administration (NARA) from atmospheric pollutants has been a matter of long time concern. This research program currently involves the study of shielding mechanisms provided by the boxboard containers commonly used in protecting archival materials from atmospheric pollutants such as sulfur dioxide and nitrogen oxides.

The diffusion constants of SO_2 and NO for six types of boxboard used to make archival boxes were measured. For the two samples provided by NARA diffusion constants were found to be about 1×10^{-3} cm^2/sec. Four samples obtained from a commercial manufacturer had diffusion constants of 3×10^{-3} cm^2/sec to less than 1×10^{-5}. These data suggest that in many cases, diffusion of SO_2 and NO through boxboard is mediated by the particular glue used to laminate the boxboard.

The absorption of SO_2 by boxboard was found to be strongly dependent upon the nature of the boxboard sample. Both permanent and nonpermanent binding of SO_2 were observed. SO_2 absorption in the range of 800 to 1600 micrograms of SO_2 per gram of boxboard was found for the NARA boxboards.

The absorption of NO by the same NARA boxboard was found to be considerably less than that of SO_2. For the two NARA boxboards studied we found less than 1 microgram of NO per gram of boxboard was absorbed.

FLUORESCENCE MONITORING OF CURING REACTION AND POLYMER PROCESSING

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The goal of this program is to apply fluorescence monitoring methods to a variety of curing systems and polymer conversion processes, and to evaluate the stability of fluorescent probes in the presence of polymerization initiators. Currently, we are addressing industrial needs identified by Enichem America, Raychem, and the NIST/industry Consortium on New Measurement Technology for Polymer Processing.

CHARACTERIZATION OF FLUORESCENT PROBES

A variety of fluorescent probes are needed for fluorescence monitoring of polymer processing. Fluorescence properties of viscosity-sensitive probes, including dansylamide, diphenylmethane and triphenylmethane, were characterized for the NIST/industry Consortium on Polymer Processing. The intrinsic fluorescence of poly(ethylene terephalate) was also characterized for the Consortium. Furthermore, in collaboration with scientists in the Dental and Medical Materials Group, fluorescence properties of some organic dyes were measured to determine their usefulness as internal standards in fluorescence cure monitoring of dental resins.

FLUORESCENCE MONITORING OF POLYURETHANE RESINS

In-line fluorescence methods and FTIR methods are being developed to meet the need for monitoring the cure of polyurethane insulation layers in solid rocket motors. The fluorescence spectra of organic dyes dissolved in polyurethane resins are sensitive to local viscosity. The excimer forming dyes are particularly useful as probes since the monomer emission can be used as an internal standard in the measurement. In this case, the probability of excimer formation is related to molecular mobility and hence to the microviscosity that changes with the degree of cure. This approach has been used to monitor the cure of hydroxy-terminated polybutadiene with isophorone diisocyanate.

FLUORESCENCE MEASUREMENT OF PROTEIN CONFORMATIONS AT THE INTERFACES OF POLY(STYRENE/ACROLEIN) LATEXES AND SOLVENT

The behavior of human serum albumin (HSA) and gamma globulin (γG) at the interfaces of poly(styrene/acrolein) latex particles and solvent was investigated at the Center of Molecular and Macromolecular Studies, Lodz, Poland under a US-Polish collaborative project with scientists at the Center. The relative amounts of proteins bound to the latex surfaces by hydrophobic adsorption and by covalent immobilization were found to be affected by the chemical composition of latex particles. Measurements of fluorescently labeled HSA and γG at interfaces of latex particles and solvent indicated that, upon attachment, protein molecules first lost their internal fluidity and only later changed their conformations.

DENTAL AND MEDICAL MATERIALS

The objective of this Group is to provide basic materials science, engineering, and test methods which may be used by sectors of the health-care industry or profession for the development of new or improved materials, delivery systems, and standards.

New monomer systems that shrink less, are more resistant to oral fluids and with the potential to bond to teeth and other materials are the object of intense investigations. These monomers may find their applications for improved dental composite restoratives, adhesives and cements. Durability is assessed by the evaluation of properties such as hardness, flexure strength, and wear resistance following immersion in food simulating liquids. Studies of the basic chemistry of calcium phosphate compounds as they relate to mineralization, demineralization and remineralization are pursued. The analysis of the failure of ceramic and ceramic-metal restorations is being conducted with the objective of defining tougher material systems. Fractography, coupled with Weibull analysis of failures, is employed. Finite element analysis and modeling of multicomponent systems is used to identify the states of stress in restorations and model test systems.

The group has extensive interactions with other organizations to further strengthen the impact of its programs. The American Dental Associations Paffenbarger Research Center maintains its staff at NIST to carry out cooperative research. The Center of Excellence for Materials Science Research at NIST, one of three such research entities currently funded by the National Institute of Dental Research, is directed by Dr. Rafael L. Bowen and co-directed by Dr. John A. Tesk, Leader of the Dental and Medical Materials Group at NIST. Five research projects are being pursued by scientists in the Dental and Medical Materials Group and the American Dental Association Health Foundation/Paffenbarger Research Center through 1994. Four research associates from the intramural research program of the National Institute of Dental Research plus guest scientists from the United States Navy and the Public Health Service form an important part of the dental program.

FY 93 Significant Accomplishments

- A bis-spiro orthocarbonate (SOC) monomer, capable of polymerization with expansion, has provided crosslinked, glassy polymers with near complete double ring opening. This represents a significant advance in the development of expanding monomers since prior to this, SOC homopolymers have been characterized by excessive leachable components, poor mechanical strength, and low glass transition temperatures.

- A series of cyclopolymerizable resins prepared by a one-step synthesis/formulation process was found to contain the greatest percentage of double bonds in the 1,6-diene configuration, which is necessary for desired cyclization.

- A polymer-supported version of the amine catalyst required for the synthesis of cyclopolymerizable monomers and resins was developed. Advantages for this approach include simplified product isolation, a completely solvent-free process, and potential recycling of the catalyst. These factors should make the production of cyclopolymerizable monomers a more attractive prospect for industry.

- Rubrene was identified as an acceptable fluorescent internal standard for cure monitoring of dental resins by fluorescence spectroscopy of resin microviscosity-sensitive probes.

- A new type of high molecular weight multifunctional urethane acrylic oligomer capable of yielding strong, tough, highly cured yet low shrinking dental polymers and composites was developed.

- Polymeric amorphous calcium phosphate composites were prepared that release calcium and phosphate ions in ratios favorable for the stabilization and/or remineralization of defective mineralized tissue. Potential applications may be found in dental sealants and orthodontic adhesives.

- In a manuscript entitled, " Error Propagation Biases in the Calculation of Indentation Fracture Toughness", a series of Monte-Carlo calculations revealed that the most reliable calculations of mode I fracture toughness, K_{IC}, can be made from the inverse slope of a regression analysis of $C^{-3/2}$ (C, indentation crack length) vs P (load) with the line forced through the origin.

- A reference calcium phosphate material, hydroxyapatite, was developed for the U.S. Food and Drug Administration (FDA).

- A patent for improved radiation-shielding materials was awarded in February 1993 and assigned to the ADAHF. These impression material-type shielding composites are currently undergoing clinical evaluation in 19 Veterans Administration hospitals.

- Several prototype alloy combinations have been tested under simulated clinical conditions and have demonstrated the feasibility of developing a mercury-free, all-metal direct-filling restorative material.

CALCIUM PHOSPHATE CHEMISTRY, BIOCHEMISTRY, STRUCTURE AND CLINICAL IMPLICATIONS AND ANALYTICAL METHODS

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Because of the relatively high solubility of amorphous calcium phosphate (ACP) compared to hydroxyapatite (HAP), it is capable of supplying high concentrations of calcium (Ca) and phosphate (PO_4) ions in ratios that favor the formation of HAP. Several visible light curable methacrylate resin composites based on the use of ACP as a filler have been evaluated for their strength and Ca/PO_4 release properties. The results to date suggest that such composites, when applied to tooth surfaces and other mineralized tissues, have the capacity to either stabilize or remineralize damaged tooth structure.

The importance of extracellular fluid supersaturation in establishing the size and arrangement of bioapatite in the extrafibrillar mineral deposits of cartilage, embryonic bone, and mantle dentin was demonstrated. Results showed that this solution parameter may also be an important factor contributing to the large disparity in size between dentin and enamel crystals.

The infrared and Raman vibrational assignments of octacalcium phosphate (OCP) were reevaluated and new assignments or reassignments of many bands were made. The study also revealed that two polymorphic forms of OCP may exist whose structures differ mainly in acidic phosphate and water bonding, and possibly in water content as well.

A project has been initiated to develop prescription fluoride formulations that use controlled hydrolysis of a complex fluoride compound in the presence of calcium to deposit a large labile fluoride reservoir in the oral environment. Successful completion of the proposed project will lead to fluoride rinses that produce the maximum protection from decay at a minimum applied dosage. Despite a lower fluoride concentration, all experimental rinses produced fluoride deposition equal to or greater than that produced by the currently used rinses.

A computer simulation of the demineralization of teeth as effected by a number of variables was developed. The results of simulations show that the effect of fluoride on the caries process is to decrease the rate of demineralization by maintaining a lower pH within the lesion.

A study to determine potential effective treatments for dentin hypersensitivity showed that the although dentin permeability was greatly reduced by treatment with an oxalate solution, permeability increased with washing because the deposit was slightly soluble in artificial saliva. Permeability decreased with washing in the samples that received treatments that deposited calcium phosphate, probably because additional insoluble deposits were formed during the washing.

Carbonic acid solutions containing high concentrations of calcium and phosphate were tested as to their efficacy in reducing dentin permeability. This acid holds calcium and phosphate in solution. When released as an aerosol, carbon dioxide escapes by evaporation, decreasing the acidity and increasing the precipitation of amorphous calcium phosphate compounds. Non-aerosol carbonated solutions can have similar properties. Results indicated that these solutions remineralized teeth and decreased dentin permeability.

A study on improving the handling properties of a self-setting calcium phosphate cement paste showed that gelatin improved the rheological properties of the material, rendering a smoother paste. The setting time was reduced by approximately a factor of two by polymerization of a monomer in the mixture. The strength immediately after setting was also improved by the polymerization of the monomer. Both additives at 10% concentration led to significantly higher strength at 24 hours.

Bad breath is caused by the production of sulfides related to bacterial metabolism in advanced periodontal disease. A microanalysis method was developed that can be applied to measure sulfide in a single periodontal pocket. Attempts are being made to develop a clinical technique that can be used to monitor the progression and remission of periodontal disease.

Pathologic cardiovascular calcification is a complex process, the precise mechanism of which is still uncertain. A study utilizing multiple techniques was undertaken to characterize the inorganic component of cardiovascular deposits. Calcific deposits that were retrieved from human aortas, carotid arteries, human heart valves, tissue-derived heart valve bioprostheses (human use) and a polyurethane total artificial heart (animal use) were characterized by chemical analyses, optical and structural techniques and by solubility measurements. The data strongly suggest octacalcium phosphate as a transient precursor in the formation of cardiovascular deposits.

A reference calcium phosphate material, hydroxyapatite, was developed for the U.S. Food and Drug Administration.

DENTAL POLYMER, COMPOSITE, CEMENT, SEALANT, AND ADHESION CHEMISTRY

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A functionalized spiro orthocarbonate (SOC) intermediate was prepared and used to obtain several bis(SOC) monomers capable of polymerization with expansion. Polymerization studies with one of these difunctional monomers has provided crosslinked, glassy polymers with near complete double ring opening. This represents a significant advance in the development of expanding monomers since prior to this, SOC homopolymers have been characterized by excessive leachable components, poor mechanical strength, and low glass transition temperatures.

A series of cyclopolymerizable resins prepared by a one-step synthesis/formulation process was characterized with regard to product distribution and the molecular weight distribution of the oligomeric components by the use of NMR and GPC analyses. Cyclopolymerizable resins with viscosities similar to those of conventional dental resins were found to contain the greatest percentage of double bonds in the 1,6-diene configuration, which is necessary for the desired cyclization.

A polymer-supported version of the amine catalyst required for the synthesis of cyclopolymerizable monomers and resins was developed. Advantages for this approach include simplified product isolation, a completely solvent-free process, and potential recycling of the catalyst. These factors should make the production of cyclopolymerizable monomers a more attractive prospect for industry.

A new type of high molecular weight multifunctional urethane methacrylate oligomer with relatively moderate viscosity was synthesized from BIS-GMA and DDI, an aliphatic diisocyanate derived from dimer acid. Some of the potential advantages of using resins based on this type of multifunctional acrylic oligomer are: (1) reduced polymerization shrinkage due to the relatively high molecular weight between vinyl groups, (2) reduced leachability and likelihood of adverse biological side effects because of the large bulk of the oligomer which on polymerization becomes even larger and less extractable and (3) better control of the final properties of the polymer because of the wide spectrum of chemical structures that can be incorporated into the prepolymer resin. Strong, tough, highly converted dental polymers and composites with minimal polymerization shrinkage may be feasible.

Strong, durable bonding to dentin is an important aspect of restorative dentistry. Many current dentin bonding systems employ relatively strong acidic pretreatments to alter or remove the smear layer created by mechanical preparation of the tooth for the restoration. These strong acidic etchants may have adverse side effects such as excessive dimineralization and denaturation of the dentural substrate. Aqueous solutions of L-ascorbic acid (Vitamin C) were shown to be mild acidic etchants, that effectively alter dentinal surfaces for subsequent bonding. Significant tensile bond strengths between ascorbic acid treated dentin and composites were obtained using several dentinal bonding resins.

The zirconyl salt of NTGGMA (the adduct of N-p-tolylglycine and glycidyl methacrylate was synthesized and shown to be an effective primer/comonomer for dentin bonding.

More than 250 restorations have been placed as part of a study of dentin and enamel bonding systems that were developed. These trials have resulted in the development of three new commercial products in the past year based on ADAHF patents. These products involve changes in chemistry and delivery methods developed during clinical evaluations. Also, three new ADAHF licensees have been added in the past year; two have introduced products to the market and the third has a product in development. The transfer of this technology to the marketplace has been largely the responsibility of the ADAHF clinical program.

Work on adhesion to hard tissues is primarily directed toward the improvement of adhesive bonding of composite restorative materials to both dentin and enamel. Using enhanced statistical data analysis and more efficient experimental designs, there has been steady progress in understanding the mechanisms and limitations of state-of-the-art adhesive bonding technologies. New monomers have been developed that penetrate the prepared dentin surface more completely before polymerizing. New techniques in the use of optical microscopy, scanning electron microscopy and transmission electron microscopy have increased the understanding of failure modes for bonded restorations. The new data will accelerate progress toward more satisfactory adhesive bonding to dentin, cementum, and enamel.

The application of protective coatings on the entire exposed surfaces of patients' teeth is likely in the foreseeable future. Transparent or aesthetic protective polymeric coatings for dentin as well as enamel are under development and have passed initial tests toward clinical application. The use of these materials should have special importance in prevention of root caries. Recent results indicate that new experimental formulations of these materials can successfully adhere to the whole tooth and withstand challenges of the oral environment.

A request for a instrumentation grant was submitted to NIH for the purchase of software and hardware to enable group scientists to envision potential restorative-material component molecules. Computer-aided research of this type will help determine reasonable avenues of research with less time-consuming and often slower bench work.

DENTAL ALLOYS, CERAMICS, METROLOGY, AND ANALYSIS

J.M. Antonucci, W. McDonough, J. A. Tesk, F. W. Wang, Da- Wei Liu, J. E. McKinney[1], K. Asaoka[2], R. L. Bowen[3], F. C. Eichmiller[3], A. A. Giuseppetti[3], L. A. George[3], J. R. Kelly[4], and R. M. Waterstrat[3].
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a) A manuscript entitled, "Influence of Tempering Method on Residual Stress in Dental Porcelain", showed that the temperature, T, at the midplane of porcelain specimens being cooled could be well described by Newton cooling with $T\text{-}T_a = Ae^{-mt}$, where T_a is the ambient temperature and m is the cooling rate exponent which is a function of the cooling method. This applied to thick specimens (greater than 6 mm) subjected to slow cooling, and for thin specimens (2 mm) subjected to fast cooling. Computer simulations of stress development were consistent in their predictions of: 1) thermal shock fracture with experimentally observed failure for specimens greater than 3 mm thick subjected to forced air convection, 2) and in predictions of surface temper compared with the experimental measurements.

b) An apparent fracture toughness, K_a (using only the relation, $K_{IC} = \chi P C^{-3/2}$ presented in the preceding) is being explored as a method for evaluation of the many variables that are possible in the design and processing of a multilayered system. The results from indents that were made over a range of loads up to 100N indicated that: 1) K_a is higher for thinner layers of the same ceramic on metal, 2) and K_a is higher for opaque porcelain on metal than for body porcelain on metal and that K_a for the body porcelain decreases at higher loads (whereas for opaque it does not), indicating different responses of opaque and body porcelain in porcelain- metal systems.

The clinical program has been actively involved in a cooperative project with NIST metallurgists in developing an all-metal direct-filling restorative material. This "amalgam-alternative" would have similar handling characteristics to present amalgams and physical properties superior to other direct-filling materials. Several prototype alloy combinations have been tested under simulated clinical conditions and have demonstrated feasibility for use as clinical restorative materials. The objective of this work is to develop a material that can be used in a manner similar to amalgam for stress-bearing posterior restorations. The clinical program will concentrate in the future on delivery methods and instrumentation for clinical use of this new technology.

NMR is an invaluable tool for structure determination after the synthesis of organic compounds. PRC and NIST scientists have an instrument available daily to identify compounds of interest to dental chemistry generally and restorative materials science specifically. The facility is also available to outside users at a minimal cost and it has become financially self-supporting.

An X-ray image magnified microradiographic technique, with synchrotron radiation, was used to study various stages of partially demineralized tooth specimens. The results showed that the technique consistently produced significantly more information on the structural features of carious lesions than that of contact microradiography, particularly in the early stages of demineralization.

During the past year, work continued on testing, characterizing and optimizing a new ADAHF-patented biocompatible alloy of zirconium, palladium and ruthenium. The material has exhibited extraordinary resistance to fracture and wear. The alloy is strong enough for dental and medical devices and holds significant potential as an industrial coating where high performance materials are required for bearing surfaces and mechanical joints.

The biaxial flexure strength test was shown to easily distinguish between composites with silanized macrofillers and those without silanization. The difference in mean strengths was at least threefold. Similarly, the microbond bead test was used to evaluate the interfacial shear strength of silanized and unsilanized E glass fibers that were treated with a visible light curable BIS-GMA resin. A threefold difference in strength was noted for silanized versus unsilanized specimens. The relatively low standard deviations inherent in these test methods allow the use of fewer samples than are usually needed to show statistically significant differences.

In a preliminary study the fluorescence changes of 4EDMAB in an experimental dental resin had been correlated with degree of cure (DC) measurements obtained from FTIR spectroscopy. The correlation indicated a monotonically increasing but nonlinear function. A major need was to identify a suitable internal standard for fluorescence measurements that would permit the assessment of DC directly from fluorescent measurements.
Rubrene was identified as an acceptable internal standard for cure monitoring of dental resins by fluorescence spectroscopy of resin microviscosity-sensitive probes.

OUTPUTS/INTERACTIONS

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G.B. McKenna, Member, Advisory Board
E.A. DiMarzio, Member, Advisory Board
Technical Agent for ATP Cooperative Agreement
Representative, External Advisory Board for ATP Cooperative Agreement

Calcified Tissue International
E.D. Eanes, Member, Editorial Board

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Center for Molecular and Microstructure of Composites
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Chemical Society of Washington
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Member, Long Range Planning Committee
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Chairman, Science Fair Committee
Member, Long Range Planning Committee

Comite International Permanent pour La Recherche Sur La Preservation des Materiaux en Milieu Marin (COIPM)
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Composite Manufacturing
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Defense Nuclear Agency
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Drexel University
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Gordon Research Conference: Science of Adhesion
    J.M. Antonucci
        Member of the Council of the Gordon Research Conferences

Gordon Research Conference: Polymer Physics
    C.C. Han, Chairman 1994

Gordon Research Conference: Calcium Phosphates
    L.C. Chow, Co-chairperson, 1992

Great Lakes Composites Consortium
    D.L. Hunston, Member, Technical Advisory Board

Institute of Electrical and Electronic Engineers (IEEE)
Conference on Electrical Insulation and Dielectric Phenomena
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        Member, Board of Directors
        Member, Executive Committee
        Chairman, Digest Committee
        Editor, Digest of Literature on Dielectrics

Interagency Oral Health Research Group
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    F.C. Eichmiller, Member

International Association for Dental Research
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        Member, Executive Committee, Dental Materials Group
        Archivist, Dental Materials Group
        Member, Souder Award Committee
    N.W. Rupp, Past President, Dental Materials Group
    J.A. Tesk, Treasurer, Dental Materials Group

International Council on Alloy Phase Diagrams
    R.M. Waterstrat, Member

International Journal of Adhesion & Adhesives
    D.L. Hunston, Member, International Advisory Editorial Board

International Standards Organization
TC106, Dental Materials and Devices

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J.A. Tesk
U.S. Expert, SC-2, WG-2; Base Metal Alloys
Member, U.S. Expert, SC-2, WG-1 on Porcelain-Metal Systems
Member, TAG
TC150, SC-2 on Cardiovascular Implants, Advisor to TAG

Journal of Alloys and Compounds
R.M. Waterstrat, Member, Editorial Board

Journal of Operative Dentistry
F.C. Eichmiller, Member, Editorial Review Board
P.S. Bennett, Member, Editorial Review Board

Journal of Polymer Science, Physics Edition
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Journal of Rheology
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Measurements for Polymer Processing Consortium
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    L.A. George, Secretary, Potomac Chapter

NIST/Industry Polymer Blends Consortium
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Industrial and Academic Interaction

Industrial

NIST is working with the **Automotive Composites Consortium (ACC) formed by Ford, Chrysler, and General Motors** to develop the technology which will make liquid composite molding the most attractive fabrication method for light-weight structural automotive parts. The technology permits the use of computer simulation rather than expensive, time consuming experiments to optimize tool design and processing conditions. NIST is using its process simulation models to predict mold filling for parts of interest to the ACC and to measure the preform permeabilities required by the analysis. The ACC provides details on the part design and feedback on the validity of the predictions from the simulation so the models can be refined and improved. Studies of an automotive front-end structure are nearly complete, and a new project on a van cross-member has begun.

General Electric and Ford Motor Company have an Advanced Technology Program that is attempting to commercialize a material system with the advantages of a thermoplastic but processes like a thermoset so that liquid composite molding can be used to make structural automotive parts. NIST's Polymers Division is supporting this effort by providing permeability measurements on the reinforcement materials to be used. These data are a key element in developing the optimized processing that is required to make the fabrication cost effective.

A cooperative program with **Grumman Corporation** is extending NIST's process simulation capability for fabrication of structural composites parts by liquid molding to commercial aerospace applications. Grumman is testing and evaluating NIST's finite element codes through comparisons with flow visualization experiments and the fabrication of parts. NIST is using the results to refine and improve the models.

An ongoing collaboration with **General Electric** is developing test methods to determine permeability for liquid composite molding. As part of this collaboration, NIST has helped GE develop high quality permeability data for the graphite fabrics used in jet engines.

Boeing Aircraft is considering the use of RTM for fabrication of a variety of aircraft parts and is taking advantage of NIST's expertise in this area. The cooperation includes process simulation models and permeability measurements. As part of this effort, a Boeing engineer, Victor Yagi, spent two weeks at NIST learning how to measure permeability, and then returned to Boeing with the NIST equipment designs.

A Cooperative Research and Development Agreement has been developed with **ViGYAN, Inc.**, to develop commercial versions of NIST's process simulation software for liquid composite molding. ViGYAN will use elements of their existing software and NIST's mold filling and graphics animation programs to create a commercial package that has a user-friendly, graphical interface, program documentation, and product support.

NIST, the **Automotive Composites Consortium (Ford, General Motors, and Chrysler), Owens Corning, and Dow Chemical Company** have initiated a joint program to study the fundamental aspects of durability for polymer composites in structural automotive applications. The goals are to improve test methods and predictive models for durability and to provide guidelines for the development of improved materials. NIST is studying environmental degradation in simple geometries like the single-fiber fragmentation test, and the ACC is investigating full composites to see how the fundamental data measured in the simple geometries translates to macroscopic composite properties. To assist the program, Owens Coring is providing glass fibers and expertise on surface treatments, while Dow Chemical Company is supplying resins and advice on sample preparation.

In cooperation with **Grumman Corporation**, a project was initiated to study how the properties of polymer composites are changed when different coatings (sizings) are applied to the fibers prior to making the composite. NIST is providing facilities to make these specially prepared materials and is measuring the fiber-matrix interface strength. Grumman is preparing the samples at NIST and testing the properties of the full composites. Durability is a property that is of particular interest in this study.

EXXON and NIST are investigating the durability of composites because they have the potential to dramatically reduce weight in off-shore oil rigs, and this will permit access to deep-water oil that is not out of reach. A key question is the degradation of the glass fiber/epoxy composites that would be used. NIST and EXXON are measuring the effect of moisture exposure on the interface using the single fiber fragmentation test. The two organizations are using different model systems and comparing the results. In addition, EXXON is conducting tests on full composites for comparison with the results for both sets of single fiber tests.

A collaborative program with **Dow Chemical Company** is investigating the effect of morphology on the fracture behavior of two-phase toughened thermosets that are important for adhesives and composites. Dow has some unique chemistry that permits the generation of materials with systematic variations in morphology. NIST is conducting fracture experiments and utilizing its expertise in toughening mechanisms to establish structure-property relationships that industry can use to formulate improved materials.

A Conference on "Passport Laminate Testing" was sponsored jointly with the U. S. Department of State. Participants from **11 companies** and four government agencies attended. The objective was to discuss the test methods currently used to evaluate the laminating materials that the government employs to protect data on passport and other such documents. Industry was given the chance to see the tests in detail and, in return, provide some valuable suggestions on improving the tests.

Under a Cooperative Research Agreement which has been signed with **Michigan Molecular Institute** (MMI) NIST is using its small angle x-ray and neutron scattering facilities to study the size and shape of polyamidoamine dendrimers synthesized at MMI.

A NIST/industry consortium, "New Measurement Technology for Polymer Processing" develops real-time measurement technology based on optical and fluorescence methods to monitor important processing parameters. Member companies include **Dow Chemical, DuPont, 3M, Rohm & Haas and Flow Vision.**

Under a Research Associate Program with **Enimont America** a fluorescence method for in-line monitoring of a microwave cure process is being developed.

The NIST Small Angle X-ray and Pole Figure Facility continues to be a resource for the U.S. Industry. Projects on various aspects of effects of processing on the SAXS measured structure of polymers were performed with **Mobil Chemical Company, Shell Oil Company. General Electric Corporation, W. R. Grace Company and Armstrong World Industries.**

Collaborative studies of the yield behavior of glassy polymers were undertaken with **Xerox.**

A guest scientist from **Xerox Corporation** is engaged in a study of the evolution of the yield response of a copolymer glass after a quench from above to below the glass transition. The copolymer, polystyrene-poly(n-butyl methacrylate), is used in toner applications and the yield stress is related to the processing of the polymer into a fine powder for toner applications.

NIST and **E. I. duPont de Nemours and Company** have initiated a joint program to study the polymer/solid interface and to address the fundamental problem of packing density and interchain diffusion near a flat substrate. DuPont is supplying specialized model materials for the study which takes advantage of the new interface characterization technique based on neutron reflectivity developed by NIST. The results of the study will help identify processing conditions that optimize interface properties in composites, coatings, adhesives, and electronic packaging systems.

A Cooperative Research and Development Agreement has been established with the **National Center for Manufacturing Science** on the nature of the two phase morphology of interpenetrating polymer networks. One of the phases is produced from sol-gel chemistry based on organo-silicon compounds. The potential applications are to produce new materials for printed wiring boards. SANS studies have already started in collaboration with **Sandia Labs**, a consortium member of NCMS.

A Cooperative Research and Development Agreement was signed with the **Dow Chemical Company** to study fracture incubation in engineering thermoplastics using SAXS and positron annihilation lifetime spectroscopy. Polymers Division staff and a foreign guest scientist collaborate with researchers from Dow to investigate incubation and growth of flows under creep loading conditions.

Collaborative research among scientists from NIST, **Eastman Chemicals** and the **Forest Products Laboratory of the USDA** investigates the morphology of cellulose triacetate and its aligomers by solid state NMR techniques.

A Cooperative Research and Development Agreement was developed among **E. I. duPont de Nemours, Co., University of Delaware** and NIST to study physical aging of Nylon®-66, This resulted in a post-doctoral level researcher, I. Spinu, working in the Polymers Division.

A Cooperative Research Agreement with **Armstrong World Industries** studies the viscoelastic properties of plasticized PVC coatings. The work will use NIST's specialized characterization facilities to study the relationship between processing conditions and properties for model material systems provided by Armstrong. There is also a program to understand viscoelasticity, as it affects extrusion and foaming of rubber foam insulation.

Collaborative research among **Goodyear, Sandia National Laboratory** and NIST on the subject of elastomer blends involves SANS studies of the chemical microstructure effects on the miscibility of elastomer blends. NIST expertise on this subject is heavily relied upon in this technologically important subject.

A NIST/Industry polymer blends consortium was initiated to study effects on polymer blend properties of mixing/demixing under shear flow as well as methods of understanding and characterizing the interface. The first consortium meeting was held September 24, 1993. At that time five companies, **Rohm and Haas, Raychem, 3M, Armstrong World Industries** and **Aristech** had formally signed agreements to join the consortium. Eight additional companies and one national laboratory were in the process of negotiating membership.

Cooperative research with **GE** on the morphology and phase separation studies of the reactive polymerization system of cyclic polymers resulted in **GE** fellow, Dr. Roger Kambour spending 8 months in the Division working with the staff on this technologically important polymer system.

Dentsply International placed a guest scientist to work in the Dental group to observe processing technology with a view toward future licensing of a patent on cyclopolymerizable monomers.

A Dental Group scientist took a lead role with American dental industry to incorporate changes to an ISO committee draft that had held classes that would have had severe negative impacts on exporting of some American dental casting alloys.

The Dental Group provided the initial leadership for efforts to form a consortium with American dental companies for the development of a mercury free, direct-filling, metallic restorative.

Two dental companies, **BISCO** and **Pulpdent**, signed agreements for licensing of adhesive technology developed by American Dental Association Health Foundation (ADAHF) in the dental group.

Jiniru Pentron provided funding to the ADAHF for work on electroposition of dental alloys.

Enamelon, a new start-up company, licensed a patent from the ADAHF for the marketing of remineralizing chewing gum.

Industrial/Academic

A cooperative research program on the subject of polyolefin blends among NIST, **Exxon** and **Princeton University** has been carried out intensively in the past two years.

NIST has been working with a group of representatives from the microelectronics community who are interested in the quality and sophistication of measurements used for characterizing properties of microelectronic packaging materials. So far, the group consists of representatives from **Semiconductor Research Corporation, IBM (Endicott), DEC, Microelectronics and Computer Technology Corporation, Cornell University, University of Texas, University of Maryland, Purdue University, and Naval Surface Warfare Center (Crane, IN).**

A conference entitled "Workshop on Fluid Flow in Liquid Composite Molding" was held September 20-22, 1993 at NIST, and was jointly sponsored by NIST, **General Electric, and Ford Motor Company**. The attendees included **30 Industry Scientists and 11 University Researchers**. The goals of the workshop were to clarify the fluid flow issues facing the industry, open lines of communication between those working on each issue, and focus attention on those issues deemed most critical at the present time. In addition to the usual posters and invited lectures by world experts, the meeting featured small discussion groups devoted to detailed examination of the major issues in the field. The groups identified the most critical challenges in each area, and this information will be used in future program planning.

Academic

Professor José Giacometti from the **University of Sao Paulo at Sao Carlos** in Brazil has participated in a study of the polarization distribution in poled films of the alternating copolymer of vinylidene cyanide and vinylacetate, a candidate host polymer for non-linear optical guest/host systems.

Professor Maria Zanin from **Universidade Federal de Sao Carlos**, Brazil participated in a study of charge distribution in clay-filled polypropylene insulator films.

A grant to **Drexel University** supports development of optical and ultrasonic techniques to measure resin flow front velocity, mold filling time, resin solidification, resin temperature, part shrinkage, and resin modulus.

Professor K. F. Lin, **National Taiwan University**, participated in the development of a fluorescence technique, based on frequency shifts, to measure curing of thermosetting resins. The approach has the advantage that no internal standard is needed.

A NATO sponsored collaborative effort with the Instifuto de Ciencia y Tecnologia de Polimeros, Madrid, Spain investigates smectic liquid crystalline polymers.

A collaborative project with the **University of Maryland Baltimore** funded by the EPA addresses the stability of well-characterized lead solutions in polycarbonate bottles. The solutions are used in toxicology studies at the **University of Maryland.**

Staff at the **University of Massachusetts Lowell** collaborates on the development of an in-line method for monitoring the uniformity of mixing in blends of recycled plastics.

Professor H. Marand of **Virginia Polytechnic Institute and State University** joins in the study of the fine texture of crystallizable polymer blends.

The measurement of domain size and stoichiometry in blends of cellulose and hydrogen-bonded polymers by solid state nuclear magnetic resonance spectroscopy is conducted jointly with **McGill University.**

A collaboration with **Tel Aviv University** investigates failure mechanisms in adhesive joints by analysis of experimental results by elasto-plastic finite element methods.

A collaborative program has been initiated with the **University of Delaware** to investigate the polymer/solid interface in composites. Pearl Chin, a PhD student of Prof. Roy L. McCullough, uses the NIST-developed neutron reflectivity technique to determine the polymer microstructure near the interface. The results will be correlated with other experiments conducted at both NIST and Delaware to assess interface properties. The goal is to provide the understanding needed to optimize the interface structure for the best composite performance.

Experimental studies of the phase diagrams and dynamics of polymer blends are conducted with collaborators from **Kyoto University, Massachusetts Institute of Technology, University of Michigan, University of Maryland, Cornell University, Princeton University, Tokyo Science University, and East China University of Chemical Technology.**

Theoretical studies of phase dynamics in polymer blends is conducted with Professor M. Muthukumar of the **University of Massachusetts.**

A joint project with Professor N. Tsutsumi of the **Kyoto Institute of Technology** investigates polymer blends as host materials for non-linear optically active guest molecules.

A joint program is underway between NIST and Prof. John Hoffman at **Johns Hopkins University** to study on-line process monitoring in liquid composite molding. As part of this effort a PhD student, Dara Woerdeman, is working at NIST to develop an evanescent-wave, optical-fiber, fluorescence measurement. This work will permit detailed measurements of the local resin behavior deep within a composite part during processing.

A joint program has been initiated with Prof. Suresh Advani at the **University of Delaware** to investigate liquid molding. The interaction involves the development of micro-flow models in an effort to predict permeability and an experimental study to visualize and model 3-dimensional flow effects in multi-layer preforms. A Postdoctoral Fellow from the University, Sridhar Ranganathan, is working at NIST on the modelling effort, while a PhD student, Tom Luce, spent the summer at NIST working on the experimental program.

NIST and **North Carolina A & T** have developed a cooperation to take advantage of NIST's expertise in liquid molding and North Carolina's capabilities in textile technology. The first step in this interaction involved several visits by faculty to NIST for discussions and a Masters student, Jeffrey Roberts, who worked in NIST's laboratories during the summer.

The Dental and Medical Materials Group participated in collaborative research efforts with scientists from the following academic institutions: The **University Louis Pasteur** (France), **Nihon University** (Japan), **Fukuoka Dental College** (Japan), **Kyushu University** (Japan), the **Rudjer Boskovic Institute** (Yugoslavia), the **University of Maryland**, the **University of Florida**, the **Oregon Health Sciences University**, **Taiwan University**, **Howard University**, the U.S. Navy Dental Research and Development Command, the **University of Strasbourg** (France), **McGill University** (Canada) and the **West China University of Medical Sciences**. Research projects including studies of stress in porcelain-metal and other dental bonded systems, new coupling agents for dental composites, postcure properties of dental composites, polymeric calcium phosphate cements, synthesis and characterization of novel fluoro and siloxane monomers and oligomers, implants biomineralization, and calcium phosphate chemistry.

Associated Activities

Invited Talks

Division personnel presented a total of 74 invited talks on research activities at the following types of organizations and symposia: industrial laboratories, 14; international symposia, 7; universities, 21; topical symposia, 1; national and government laboratories, 2; professional society meetings, 25; and Gordon Conferences, 4.

Patents

Method for Detecting Polymer Solidification during Injection Molding. A.J. Bur, F.W. Wang, C.L. Thomas and J. Rose, (Pending)

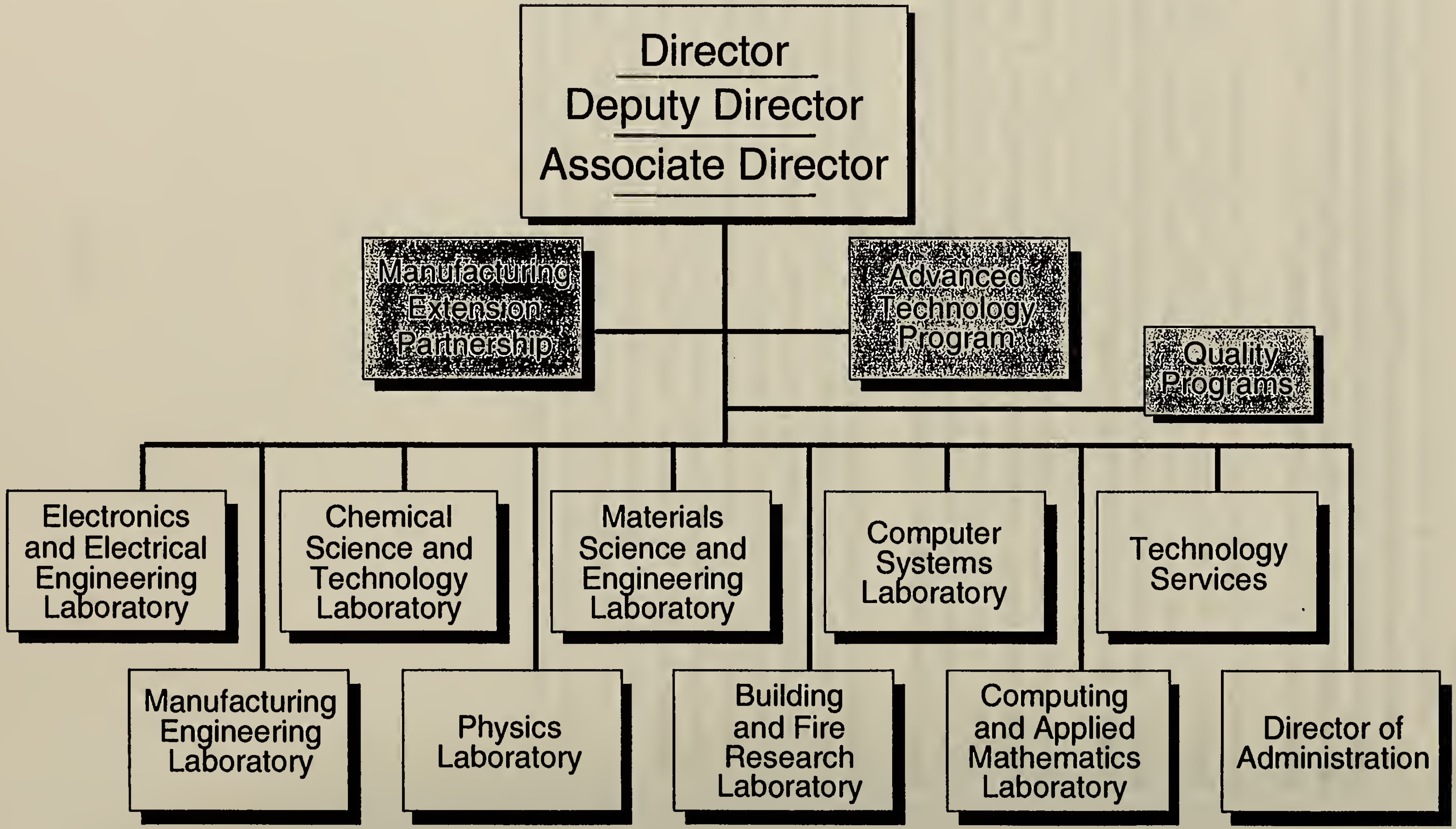
Novel Multifunctional Acrylates and the Synthesis Thereof. J.M. Antonucci, J.W. Stansbury, and Guo Wei Cheng, Patent filed, PTO serial number 828,316.

Hydrofluoroalkyl-Substituted Styrenes and Polymeric Compositions Containing Same., C.C. Han, Y. Feng and M. He, Patent filed, PTO serial no. 985,932.

Monomers for Double Ring-Opening Polymerization with Expansion., J.W. Stansbury, Patent filed, PTO serial no. 846,480.

National Institute of Standards and Technology

Organizational Chart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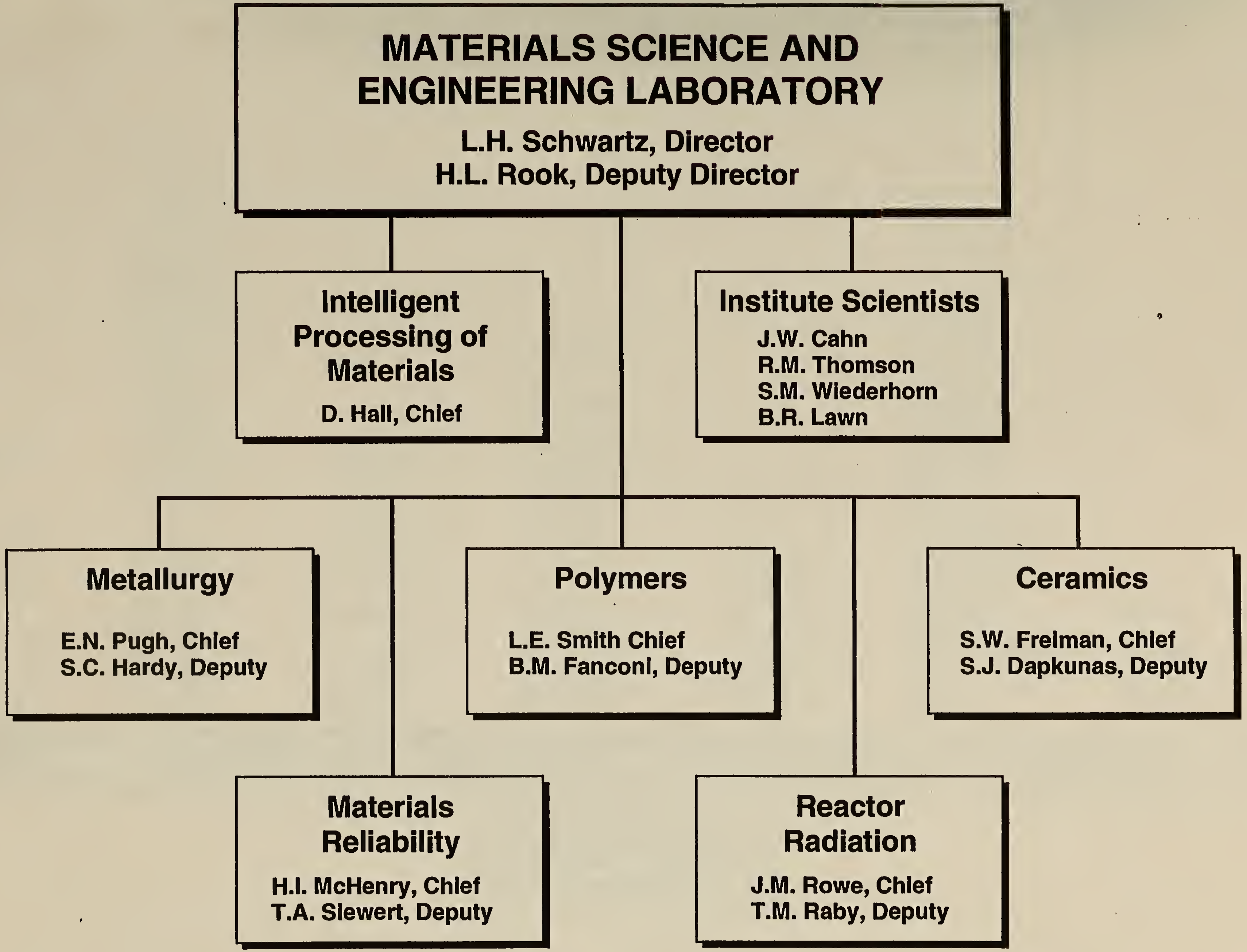

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